

EGE UNIVERSITY

DOCTORATE THESIS

**INVESTIGATION OF THE HEMICELLULOSE IN THE
STRUCTURE OF PLANT BIOMASS AND EXTRACTIVE
MATERIALS BEHAVIOUR BY USING OF MODEL
COMPOUNDS IN SUPERCRITICAL WATER GASIFICATION**

Dilek GÖKKAYA

**Supervisor: Prof. Dr. Levent BALLİCE
Co-supervisor: Prof. Dr. Mehmet SAĞLAM**

Department of Chemical Engineering

Department Code: 603.01.00

Presentation Date: 24.02.15

Bornova/İZMİR

2015

**EGE UNIVERSITY GRADUATE SCHOOL
OF NATURAL AND APPLIED SCIENCE**

(DOCTORATE THESIS)

**INVESTIGATION OF THE HEMICELLULOSE IN THE
STRUCTURE OF PLANT BIOMASS AND EXTRACTIVE
MATERIALS BEHAVIOUR BY USING OF MODEL
COMPOUNDS IN SUPERCRITICAL WATER GASIFICATION**

Dilek GÖKKAYA

**Supervisor: Prof. Dr. Levent BALLİCE
Co-supervisor: Prof. Dr. Mehmet SAĞLAM**

Department of Chemical Engineering

**Department Code: 603.01.00
Presentation Date: 24.02.15**

Bornova/İZMİR

2015

Dilek Gökkaya tarafından doktora tezi olarak sunulan “**Investigation of the Hemicellulose in the Structure of Plant Biomass and Extractive Materials Behaviour by Using of Model Compounds in Supercritical Water Gasification**” başlıklı bu çalışma E.Ü. Lisansüstü Eğitim ve Öğretim Yönetmeliği ile E.Ü. Fen Bilimleri Enstitüsü Eğitim ve Öğretim Yönergesi’nin ilgili hükümleri uyarınca tarafımızdan değerlendirilerek savunmaya değer bulunmuş ve 18/03/2015 tarihinde yapılan tez savunma sınavında aday oybirliği/oyçokluğu ile başarılı bulunmuştur.

Jüri Üyeleri:

İmza

Jüri Başkanı :

Raportör Üye :

Üye :

Üye :

Üye :

EGE ÜNİVERSİTESİ FEN BİLİMLERİ ENSTİTÜSÜ
ETİK KURALLARA UYGUNLUK BEYANI

E.Ü. Lisansüstü Eğitim ve Öğretim Yönetmeliğinin ilgili hükümleri uyarınca Yüksek Lisans Tezi / Doktora Tezi olarak sunduğum “**Investigation of the Hemicellulose in the Structure of Plant Biomass and Extractive Materials Behaviour by Using of Model Compounds in Supercritical Water Gasification**” başlıklı bu tezin kendi çalışmam olduğunu, sunduğum tüm sonuç, doküman, bilgi ve belgeleri bizzat ve bu tez çalışması kapsamında elde ettiğimi, bu tez çalışmasıyla elde edilmeyen bütün bilgi ve yorumlara atıf yaptığımı ve bunları kaynaklar listesinde usulüne uygun olarak verdiğimi, tez çalışması ve yazımı sırasında patent ve telif haklarını ihlal edici bir davranışımın olmadığını, bu tezin herhangi bir bölümünü bu üniversite veya diğer bir üniversitede başka bir tez çalışması içinde sunmadığımı, bu tezin planlanmasından yazımına kadar bütün safhalarda bilimsel etik kurallarına uygun olarak davrandığımı ve aksinin ortaya çıkması durumunda her türlü yasal sonucu kabul edeceğimi beyan ederim.

19 /02/2015

Dilek Gökkaya

ÖZET**LİGNOSELÜLOZİK BİYOKÜTLE YAPISINDAKİ HEMİSELÜLOZ VE
EKSTRAKTİF MADDELERİN SÜPERKRİTİK SU İLE
GAZLAŞTIRILMASINDAKİ DAVRANIŞLARININ BAZI MODEL
BİLEŞİKLER YARDIMI İLE İNCELENMESİ**

GÖKKAYA, Dilek

Doktora Tezi, Kimyasal Teknolojiler Anabilim Dalı

Tez Danışmanı: Prof. Dr. Levent Ballice

İkinci Danışman: Prof. Dr. Mehmet Sağlam

Şubat 2015, 192 sayfa

Temiz enerji kaynağı olarak kullanılabilecek Hidrojen ve Metan'ın Hidrotermal Gazlaşma ile lignoselülozik biyokütlelerden üretimi, gelişmekte olan yeni bir teknolojidir. Bitki yapısındaki selüloz, lignin, hemiselüloz ve ekstraktif maddeler, hidrotermal gazlaştırmada farklı farklı davranış gösterirler. Bu nedenle gazlaşma veriminde ve ürün dağılımında çok önemli farklılıklar gözlenir. Fakat bitkinin önemli kısmını (1/3) oluşturan hemiselüloz ve ekstraktiflerle ilgili literatürde yeterli çalışmanın olmaması önemli bir eksiklikler. Bu noktadan hareketle bu projede; bitki yapısındaki hemiselülozu oluşturan ksiloz, arabinoz ve pektin ile ekstraktifleri oluşturan tannik asit, gallik asit, pirogallol ve floroglusinol ile hidrotermal gazlaştırma yöntemiyle hidrojen ve metan üretilebilme imkanları araştırılmıştır. Maksimum H_2 ve CH_4 oluşumuna reaksiyon sıcaklığının, reaksiyon basıncının ve katalizörün etkisi incelenmiştir. Gaz, sıvı ve katı ürün verimleri ve sıvı ürün bileşimi; GC, HPLC, TOC, SSM cihazları kullanılarak belirlenmiştir. Reaksiyon sıcaklığının artmasıyla gaz verimi, H_2 ve CH_4 miktarı artmış, reaksiyon basıncının artmasıyla da gaz verimi ve H_2 miktarı azalmış, CH_4 miktarı ise artmıştır.

Anahtar sözcükler: Kritik Üstü Su Gazlaştırması, Biyokütle, Enerji, Hidrojen, Metan

ABSTRACT**INVESTIGATION OF THE HEMICELLULOSE IN THE STRUCTURE
OF PLANT BIOMASS AND EXTRACTIVE MATERIALS BEHAVIOUR
BY USING OF MODEL COMPOUNDS IN SUPERCRITICAL WATER
GASIFICATION**

GÖKKAYA, Dilek

PhD in Department of Chemical Engineering

Supervisor: Prof. Dr. Levent Ballice

Co-supervisor: Prof. Dr. Mehmet Sağlam

February, 2015, 192 pages

Production of Hydrogen and Methane which are used as clean energy sources by hydrothermal gasification from the lignocellulosic biomasses is a novel and developing technology. Cellulose, lignin, hemicelluloses, and extractive substances show different attitudes in hydrothermal gasification. For this reason, significant varieties are observed in the gasification yields and product distributions. In a research of literature, it was found that, there is not enough work being carried out with the hemicelluloses and extractives which are approximately 1/3 of a plant, and this is a significant deficiency in literature. From this point, in this study, xylose, arabinose, and pectin as model compounds for the hemicellulose, whereas tannic acid, gallic acid, phloroglucinol, and pyrogallol for extractives were studied. The yields of gas, liquid, and solid products were identified with the analyses using GC, HPLC, TOC, and SSM. The effect of the reaction temperature, the reaction pressure, and catalyst were investigated to reach the maximum yields of H_2 and CH_4 . As the reaction temperature increased, the gaseous product yield and the amount of H_2 and CH_4 in unit of mol increases. The increment in reaction pressure causes a decrease in the gaseous product yield and the amount of H_2 in mol, on the other hand it promotes the CH_4 amount in mol.

Keywords: Supercritical water gasification, biomass, energy, hydrogen, methane

ACKNOWLEDGEMENT

First of all, I would like to express my deepest gratitude to Prof. Dr. Mehmet Sağlam, Prof. Dr. Mithat Yüksel, and Prof. Dr. Levent Ballice, my supervisors for all I have learned from them and for their continuous help and support in all stages of my dissertation work. The things that I have learned from them will guide me for all my future working experiences.

I would also like to thank the members of my PhD committee, Prof. Dr. Nalan Kabay and Prof. Dr. Kadir Yurdakoç for their valuable suggestions and advices. In addition, I would like to thank Mr. Gürsel Serin for his technical contribution, which helped me to solve problems running the experiments. I would also like to thank Asst. Prof. Dr. Murat Sert for his support throughout my experimental studies.

I want to acknowledge the financial support for this study provided by the Scientific and Technological Research Council of Turkey (TUBITAK) in the form of research project No. 109M284.

My gratitude goes to my little daughter for her magnificent smile and to my husband, for their continuous love and their support in my decisions. As well, thanks going to my mother, my family, and my friends who have always believed in me and supported me in all my endeavors. Finally, a special dedication to my father, Prof. Dr. Ahmet Saim Selvi. who first introduced me to the world of research, transmitted me to academic life, and has always encouraged me throughout my life. Without the love and patience of my family none of this would have been possible.

TABLE OF CONTENTS

	<u>Page</u>
ÖZET	vii
ABSTRACT.....	ix
ACKNOWLEDGEMENT	xi
LIST OF FIGURES	xv
LIST OF TABLES	xx
LIST OF ABBREVIATIONS.....	xxv
1.INTRODUCTION.....	1
2.GENERAL INFORMATION.....	5
2.1Status of the Energy in the World.....	5
2.1.1 Renewable Energy.....	8
2.2 Status of the Energy in Turkey	15
2.3 CHEMICAL COMPOSITION OF BIOMASS	21
2.3.1 Cellulose.....	25
2.3.2 Hemicellulose and Pectin	26
2.3.3 Lignin	31
2.3.4 Extractives	33
2.3.5 Ash.....	36
2.4 Biomass Conversion Technologies.....	36
2.4.1 Thermochemical Conversions	38
2.5 Supercritical Water Gasification	44
2.5.1 Thermophysical Properties of Water at Hydrothermal Conditions	46

TABLE OF CONTENTS (continued)

	<u>Page</u>
3. LITERATURE REVIEW.....	53
4. EXPERIMENTAL APPARATUS AND PROCEDURE.....	67
4.1 EXPERIMENTAL.....	67
4.2 ANALYSES.....	71
4.2.1 Gas Phase Analysis.....	72
4.2.2 Liquid Phase Analysis.....	73
4.2.3 Analysis of Solid Residue and Sample	77
5. Evaluation of Results	78
5.1 Influence of Temperature and Catalyst on the Product Distribution and Gas Composition	80
5.2 Influence of Pressure and Catalyst on the Gasification and Gas Composition	110
5.3 Influence of Temperature, Pressure, and Catalyst on the Liquid Product Distribution.....	133
5.4 Evaluation of Possible Structural Changes in Activated Carbon Catalysts after Supercritical Water Gasification	173
6.0 CONCLUSION	175
REFERENCES.....	180
RESUME.....	193
APPENDICES.....	

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
2.1.1 Global energy systems transition, 1850–2150 (Dunn, 2002).....	5
2.2.1 Turkey's total primary energy production and consumption during 1990 and 2011(Mtoe)	16
2.2.2 The share of energy sources used for electricity production in Turkey-2011.	16
2.3.1 Schematic presentation of the biomass major components.....	21
2.3.2 Schematic presentation of the plant cell wall.	22
2.3.3 Composition of lignocellulosic biomass.....	24
2.5.1 Change of some water properties with Temperature and Pressure.....	44
2.5.1.1 Phase diagram of water.....	47
3.1 Simplified reaction scheme of liquifaction and/or gasification with regards to the identified key compounds and the findings from experiments with model compound.....	55
4.1.1 Schematic diagram of the SCWG system.....	68
4.1.2 Heater and autoclave batch system.	69
4.1.3 Experimental procedure for the analysis of the products.....	70
5.1.1 Temperature and catalyst effects on gas product yields of xylose and arabinose hydrothermal gasification.....	82
5.1.4 Temperature and catalyst effects on gas product yields of pectin and galacturonic acid hydrothermal gasification.....	86

LIST OF FIGURES (continued)

<u>Figure</u>	<u>Page</u>
5.1.5 Temperature and catalyst effects on hydrogen yields of xylose and arabinose hydrothermal gasification.	87
5.1.6 Temperature and catalyst effects on hydrogen yields of tannic acid and gallic acid.	85
5.1.7 Temperature and catalyst effects on hydrogen yields of phloroglucinol and pyrogallol.	88
5.1.8 Temperature and catalyst effects on hydrogen yields of pectin and galacturonic acid hydrothermalgasification.....	89
5.1.9 Temperature and catalyst effects on methane yields of xylose and arabinose hydrothermal gasification.	90
5.1.10 Temperature and catalyst effects on methane yields of tannic acid and gallic acid.....	91
5.1.11 Temperature and catalyst effects on methane yields of phloroglucinol and pyrogallol hydrothermal gasification.....	92
5.1.12 Temperature and catalyst effects on methane yields of pectin and galacturonic acid hydrothermal gasification.	93
5.1.13 Temperature and catalyst effects on carbondioxide yields of xylose and arabinose hydrothermal gasification.	94
5.1.14 Temperature and catalyst effects on carbondioxide yields of tannic acid and gallic acid.....	95
5.1.15 Temperature and catalyst effects on carbondioxide yields of phloroglucinol and pyrogallol.....	96
5.1.16 Temperature and catalyst effects on carbondioxide yields of pectin and galacturonic acid hydrothermal gasification.....	97

LIST OF FIGURES (continued)

<u>Figure</u>	<u>Page</u>
5.1.17 Temperature and catalyst effects on C ₂ -C ₄ yields of xylose and arabinose hydrothermal gasification.	98
5.1.18 Temperature and catalyst effects on C ₂ -C ₄ yields of tannic acid and gallic acid.....	99
5.1.19 Temperature and catalyst effects on C ₂ -C ₄ yields of phloroglucinol and pyrogallol.....	100
5.1.20 Temperature and catalyst effects on C ₂ -C ₄ yields of pectin and galacturonic acid hydrothermal gasification.	101
5.1.21 Temperature and catalyst effects on coke yields of xylose and arabinose hydrothermal gasification.....	102
5.1.22 Temperature and catalyst effects on coke yields of tannic acid and gallic acid.	103
5.1.23 Temperature and catalyst effects on coke yields of phloroglucinol and pyrogallol.....	104
5.1.24 Temperature and catalyst effects on coke yields of pectin and galacturonic acid hydrothermal gasification.....	105
5.1.25 Temperature and catalyst effects on TOC (mg/L) of xylose and arabinose hydrothermal gasification.	106
5.1.26 Temperature and catalyst effects on TOC yields (mg/L) of tannic acid and gallic acid.....	107
5.1.27 Temperature and catalyst effects on TOC yields (mg/L) of phloroglucinol and pyrogallol.....	108
5.1.28 Temperature and catalyst effects on TOC (mg/L) of pectin and galacturonic acid hydrothermal gasification.....	109

LIST OF FIGURES (continued)

<u>Figure</u>	<u>Page</u>
5.2.2 Pressure effect on hydrogen yield of xylose hydrothermal gasification in the presence and absence of K_2CO_3	113
5.2.3 Pressure effect on methane yield of xylose hydrothermal gasification in the presence and absence of K_2CO_3	114
5.2.4 Pressure effect on gas yield of arabinose hydrothermal gasification in the presence and absence of K_2CO_3	115
5.2.5 Pressure effect on hydrogen yield of arabinose hydrothermal gasification in the presence and absence of K_2CO_3	116
5.2.6 Pressure effect on methane yield of arabinose hydrothermal gasification in the presence and absence of K_2CO_3	117
5.2.7 Pressure effect on gas yield of tannic acid hydrothermal gasification in the presence and absence of K_2CO_3	118
5.2.8 Pressure effect on hydrogen yield of tannic acid hydrothermal gasification in the presence and absence of K_2CO_3	119
5.2.9 Pressure effect on methane yield of tannic acid hydrothermal gasification in the presence and absence of K_2CO_3	120
5.2.10 Pressure effect on gas yield of gallic acid hydrothermal gasification in the presence and absence of K_2CO_3	121
5.2.11 Pressure effect on hydrogen yield of gallic acid hydrothermal gasification in the presence and absence of K_2CO_3	122
5.2.12 Pressure effect on methane yield of gallic acid hydrothermal gasification in the presence and absence of K_2CO_3	123

LIST OF FIGURES (continued)

<u>Figure</u>	<u>Page</u>
5.2.14 Pressure effect on hydrogen yield of phloroglucinol hydrothermal gasification in the presence and absence of K_2CO_3	125
5.2.15 Pressure effect on methane yield of phloroglucinol hydrothermal gasification in the presence and absence of K_2CO_3	126
5.2.16 Pressure effect on gas yield of pyrogallol hydrothermal gasification in the presence and absence of K_2CO_3	127
5.2.17 Pressure effect on hydrogen yield of pyrogallol hydrothermal gasification in the presence and absence of K_2CO_3	128
5.2.18 Pressure effect on methane yield of pyrogallol hydrothermal gasification in the presence and absence of K_2CO_3	129
5.2.19 Pressure effect on gas yield of pectin hydrothermal gasification in the presence and absence of K_2CO_3	130
5.2.20 Pressure effect on hydrogen yield of pectin hydrothermal gasification in the presence and absence of K_2CO_3	131
5.2.21 Pressure effect on methane yield of pectin hydrothermal gasification in the presence and absence of K_2CO_3	132
5.3.1 Proposed reaction mechanism for gasification of xylose by supercritical water.	136

LIST OF TABLES

<u>Table</u>	<u>Page</u>
2.1.1 Key indicators for 1993, 2011 and 2020.....	6
2.1.2 Status of the Energy in the World.....	7
2.2.1 Energy outlook of Turkey.....	15
2.2.2 Economically feasible hydropower potential of Turkey's major river basins in 2006.....	18
2.2.3 Average solar energy potential of Turkey and insolation durations on monthly basis	18
2.2.4 Technical wind energy potential by regions in Turkey.	19
2.2.5 Total annual and Energy potential in Turkey.....	19
2.2.6 Total annual agricultural potential in Turkey.....	20
2.3.1 Typical compositions of different biomass species.	23
2.3.2 Typical compositions of different biomass species.	23
2.3.2.1 Comparision of the cellulose and hemicelluloses properties.....	27
2.3.2.2 Hemicellulose compositions of different biomass species	28
2.3.2.3 Major Hemicellulose Components.....	29
2.3.4.1 Tannin percentages in some selected plants.....	35
2.4.1.1. The most important gasification reactions.....	43
2.5.1 Physical properties change of water with temperature and pressure.	45
2.5.2 A comparison of energy conversion efficiency of different options for biomass conversion.....	46
4.1.1 Used materials in the experiments.	67

LIST OF TABLES (continued)

<u>Table</u>	<u>Page</u>
4.2.1. Equipments used in analyses of biomass and SCW products.....	71
4.2.1.1 Technical features and operating conditions of HP GC 7890A gas chromatography.	73
4.2.2.1 Technical features and operating conditions of HPLC for Method I.	75
4.2.2.2 Technical features and operating conditions of HPLC for Method II.	75
4.2.2.3 HPLC Standards Analysed by Method I and Method II were given below.	76
5.1 Experimental Plan.....	79
5.3.1. Concentrations of major organic compounds identified in liquid product from the gasification of xylose in relation to catalyst and temperature.	138
5.3.2. Concentrations of major organic compounds identified in liquid product from the gasification of xylose in relation to catalyst and temperature.....	139
5.3.3 Concentrations of major organic compounds identified in liquid product from the gasification of xylose in relation to pressure for the reaction temperature of 400°C.	140
5.3.4 Concentrations of major organic compounds identified in liquid product from the gasification of xylose in relation to pressure for the reaction temperature of 500°C.	141
5.3.5 Concentrations of major organic compounds identified in liquid product from the gasification of xylose in relation to pressure for the reaction temperature of 600°C.	142

LIST OF TABLES (continued)

<u>Table</u>	<u>Page</u>
5.3.7 Concentrations of major organic compounds identified in liquid product from the gasification of arabinose in relation to catalyst and temperature.....	144
5.3.8 Concentrations of major organic compounds identified in liquid product from the gasification of arabinose in relation to pressure for the reaction temperature of 400°C.....	145
5.3.9 Concentrations of major organic compounds identified in liquid product from the gasification of arabinose in relation to pressure for the reaction temperature of 500°C.....	146
5.3.10 Concentrations of major organic compounds identified in liquid product from the gasification of arabinose in relation to pressure for the reaction temperature of 600°C.	147
5.3.11. Concentrations of major organic compounds identified in liquid product from the gasification of tannic acid in relation to catalyst and temperature.	148
5.3.12. Concentrations of major organic compounds identified in liquid product from the gasification of tannic acid in relation to catalyst and temperature.....	149
5.3.13 Concentrations of major organic compounds identified in liquid product from the gasification of tannic acid in relation to pressure for the reaction temperature of 400°C.	150
5.3.14 Concentrations of major organic compounds identified in liquid product from the gasification of tannic acid in relation to pressure for the reaction temperature of 500°C.	151

LIST OF TABLES (continued)

<u>Table</u>	<u>Page</u>
5.3.16 Concentrations of major organic compounds identified in liquid product from the gasification of gallic acid in relation to catalyst and temperature.	153
5.3.17 Concentrations of major organic compounds identified in liquid product from the gasification of gallic acid in relation to pressure for the reaction temperature of 400°C.	154
5.3.18 Concentrations of major organic compounds identified in liquid product from the gasification of gallic acid in relation to pressure for the reaction temperature of 500°C.....	155
5.3.19 Concentrations of major organic compounds identified in liquid product from the gasification of gallic acid in relation to pressure for the reaction temperature of 600°C.....	156
5.3.20 Concentrations of major organic compounds identified in liquid product from the gasification of phloroglucinol in relation to catalyst and temperature.....	157
5.3.21 Concentrations of major organic compounds identified in liquid product from the gasification of phloroglucinol in relation to pressure for the reaction temperature of 400°C.	158
5.3.22 Concentrations of major organic compounds identified in liquid product from the gasification of phloroglucinol in relation to pressure for the reaction temperature of 500°C.	159
5.3.23 Concentrations of major organic compounds identified in liquid product from the gasification of phloroglucinol in relation to pressure for the reaction temperature of 600°C.....	160

LIST OF TABLES (continued)

<u>Table</u>	<u>Page</u>
5.3.28 Concentrations of major organic compounds identified in liquid product from the gasification of pectin in relation to catalyst and temperature.	165
5.3.29 Concentrations of major organic compounds identified in liquid product from the gasification of pectin in relation to pressure for the reaction temperature of 400°C.....	166
5.3.30 Concentrations of major organic compounds identified in liquid product from the gasification of pectin in relation to pressure for the reaction temperature of 500°C.	167
5.3.31 Concentrations of major organic compounds identified in liquid product from the gasification of pectin in relation to pressure for the reaction temperature of 600°C.	168
5.3.32 Concentrations of major organic compounds identified in liquid product from the gasification of galacturonic acid in relation to catalyst and temperature.....	169
5.3.33 Concentrations of major organic compounds identified in liquid product from the gasification of galacturonic acid in relation to pressure for the reaction temperature of 400°C.	170
5.3.34 Concentrations of major organic compounds identified in liquid product from the gasification of galacturonic acid in relation to pressure for the reaction temperature of 500°C.....	171
5.3.35 Concentrations of major organic compounds identified in liquid product from the gasification of galacturonic acid in relation to pressure for the reaction temperature of 600°C.	172

LIST OF ABBREVIATIONS

bcm:	Billion cubic meter
CGE:	Carbon gasification efficiency (moles of carbon recovered in the gas per mole of carbon in the feed)
GE:	Gasification efficiency
GC:	Gas chromatography
Gt:	Giga tonnes
HPLC:	High pressure liquid chromatography
kWh:	kilowatt-hour
MJ:	Megajoules
Mt:	Million tons
Mtoe:	Million tones of oil equivalent
P:	Reactor pressure (bar)
ppm:	parts per million
TOC:	Total organic carbon
SCW:	Supercritical water
SCWG:	Supercritical water gasification
SEM:	Scanning electron microscopy
SSM:	Solid sample module
T:	Reactor temperature (°C)
WGS:	Water gas shift
Δh_{rxn} :	Enthalpy of reaction (kJ mol ⁻¹)

1.0 INTRODUCTION

Nowadays approximately 90 % of the world energy resources consumed in the world come from coal, petroleum, and natural gas. These resources are also being depleted by the chemical industries in large measures. These reserves which have limited reservations are being depleted rapidly. Furthermore, important environmental issues are occurring. Because of these reasons and increasing levels of greenhouse pollution and toxic gas content like CO₂, SO₂, and NO_x from the combustion of fossil fuels and new alternative resources need to be developed.

Hydrogen has been identified as the most attractive and developing renewable energy carrier in the world. Researchers are developing a wide range of technologies to produce hydrogen economically from a variety of resources without having a negative effect on the environment. In these resources, biomass being CO₂ neutral and a readily available source of energy is considered to be renewable. For these and other reasons, hydrogen production from lignocellulosic biomasses (waste and residue of plant biomass) instead of conventional production is of great importance. Several processes have been explored to produce hydrogen from the lignocellulosic biomasses. In the last two decades, a novel gasification technology called supercritical water gasification (SCWG) has been developed, in which water having a pressure of over 22.1 MPa and a temperature of over 374°C (i.e. supercritical conditions) is used as the gasifying agent.

Organic parts of the biomass materials react with its water contents and decompose in a large extent to gas products, partially water soluble organics, small amount of tars and coke. Major fractions of gas products are CO₂, H₂, and CH₄, and besides these fractions, small amounts of CO and C₂-C₄ hydrocarbons are also formed. Aqueous solutions containing different organic matters such as, formic acid, carboxylic acids, hydroxyacetic acid, alcohols, aldehydes and ketones, furfural, methyl furfural, 5-hydroxymethylfurfural and phenols, and solid matters (coke and tar) are formed during the transformation process. Achieving a maximum conversion and gas yield with a high H₂ and CH₄ content, and obtaining minimum tar and coke formations depend firstly on the type of

biomass, reaction temperature and pressure, catalyst type in use and other reaction parameters.

Plant biomass generally has a complex structure and is mainly composed of cellulose, hemicelluloses, lignin, extractives, and ash forming inorganic materials. Cellulose is a polysaccharide consisting of a linear chain of β -D glucose units. The cellulose structure is the same for all plants, but only the average molecular weights can be different.

Hemicelluloses, which are a stable carbohydrate polysaccharide, are part of that fall outside of cellulose of the polysaccharides which form the cell wall. They are the second abundant biopolymer next to cellulose. A 4-5% soluble portion in cold alkaline solution of the plant is referred to as hemicelluloses according to the opinion adopted in the literature. Hemicelluloses isolation is done at low temperatures within alkali solutions, but generally with unsatisfactory yields (% 4-5) (Bogleter, 1994). While the degree of polymerization (DP) for the cellulose is in the range of 5000-10000, this range decreases to 150 for the hemicelluloses. Long chained and amorphous biopolymer hemicelluloses are composed of the primary monomer constituents, hexoses (glucose, galactose, mannose, glucuronic acid and galacturonic acid), pentoses (xylose, arabinose) (Pacheco, 2009). Within the plant, these monomers which are forming homopolymer (glucan, mannan, galactan, xylan, arabinan etc.) or copolymer (glucomannan, arabinogalactan, etc.) structures are linked to lignin or cellulose by chemical bonds and thus fixed in the fiber structure (Bogleter, 1994). The lower chemical and thermal stability of hemicellulose compared to cellulose can also be attributed to the lower degree of polymerization. Hemicellulose exists in biomass in different compositions and structures containing irregular side chains. For example pine wood hemicellulose (31 %) contains 17% glucomannan, 11% gluco-arabino-xylan and 3% galactan. Poplar wood contains 7 % glucomannan, 23% gluco-arabino-xylan and 0% galactan. Fir tree contains 21% glucomannan, 6% gluco-arabino-xylan and 4% galactan.

Lignin is a very complex high molecular weight compound with three most prevalent monomers as p-coumaric alcohol, coniferyl alcohol, and sinapyl alcohol proportions (Carrier et al., 2012). Extractives are proteins, triglycerides,

organic acids, waxes, carotene, sugars, starch and tannin etc. Lignin and extractives vary depending on the type of biomass. Also inorganic structure of biomass contains alkalies and oxides, carbonates, chlorides sulfates etc., compounds of the d-groups elements.

Substances such as protein, triglycerides, ethereal oils, organic acids, waxes, carotene, sugars, polysaccharide, and tannins fall into the group of substances which can be extracted. Cellulose, lignin, hemicelluloses, and extractive substances show different attitude in hydrothermal gasification. Therefore, important disparities are observed in the biomass and model compounds gasification reactions of hydrogen and methane, and the product distribution.

There are a variety of compounds in the inorganic parts of plants such as oxides, carbonates, chlorines of alkali, alkaline earth metals, and group d-elements. The main components in the plant structure and each one of the organic substances forming the structure have different chemical behaviours in hydrothermal gasification. So that the H_2 and CH_4 formation reactions do not occur exactly. The H_2 and CH_4 formation in the biomass and model compounds occur at different rates. In addition to the differences in the product gas composition, the type and quantity of organics in the liquid product formed through the reaction also vary. The plant type also affects the formation of coke. Except for the material that attends to reactions, the reaction temperature, pressure, and the type of catalyst used affect the formation of the maximum value of H_2 and CH_4 . Intensive studies of the hydrothermal gasification and the purpose of the industrial feasibility of the method made by research groups in many countries, mainly in the USA, England, Germany, and Japan, have increase in the last 30 years. These studies are being carried out in the laboratory and pilot level. They are being made using the model substances consist of the different biomass samples and the main components in the biomass. The important parts of the scientific research are fevered to understand the attitude of the main components in the plant structure in hydrothermal gasification and to clarify the reaction progress and determine optimum reaction conditions to obtain maximum hydrogen and methane yields. Most studies, appearing in literature, are accomplished with cellulose which is the main constituent of plants and the

glucose, monosaccharide as the model compounds. Also, the reaction mechanisms were studied to clarify by research groups. The other group works were performed with the lignin, the main important constituent of plants, the phenol representing lignin, and 1,2 dihydroxybenzene. However, any study carried out with the hemicellulose, the other main constituent of plants or monosaccharide forming hemicellulose, did not appeared in literature. Only a few studies, which were not very comprehensive, appeared regarding xylan polysaccharide and xylose. It is an important deficiency not to know the attitude and the reaction progress of the hemicelluloses and extractives, forming about one third of a plant in SCWG. In this respect, hemicellulose was isolated from poplar, pine, and fir and glucose, mannose, and galactose were selected as the model compound for hexosan is being one of the structural units in hemicellulose, and xyloz, arabinose from the pentosan compound and galactronic acid as a model compound for pectins, were studied by Salam (2013) in a TUBITAK Project (TUBITAK, Project No: 109M284).

In this study, xylose, arabinose and pectin were used as model compounds for the hemicellulose, and tannic acid, gallic acid, 1,2,3 trihidroksibenzene, and 1,3,5 trihidroksibenzene for the extractives were studied. Xylose and arabinose studies were completed in the TUBITAK Project (Saglam, 2013). Hydrothermal gasification was performed in a batch reactor system at temperature and pressure ranges of 400, 500 and 600°C and 20, 27.5, 35.0 and 42.5 MPa. Also xylose, arabinose and tannic acid were studied at 400, 500 and 600°C in the presence of, KOH, activated carbon-Ni and activated carbon-Ru. Gallic acid, 1,2,3 trihidroksibenzene, 1,3,5 trihidroksibenzene and pectin were studied at 400, 500 and 600°C in the presence of K₂CO₃ and KOH. Galacturonic acid results, were completed in the TUBITAK Project (Saglam, 2013), were used to compare with the pectin results. The objective of this study was to elucidate the simultaneous effect of the high reaction temperature, high pressure and catalyst on the gas and liquid product distribution. The influences of temperature, pressure and catalyst were examined in relation to the maximum yields of the H₂ and CH₄ gases and the liquid products of furfurals, aldehydes and carboxylic acids by gas and liquid chromatographic techniques.

2.0 GENERAL INFORMATION

2.1 Status of the Energy in the World

Main energy problem in the world is that fast degradation of non-renewable sources in terms of fossil fuels. The world has been slowly shifting from one form of energy to another—from solids to liquids and to gases since the mid-19th century, as Dunn (2002) has illustrated (Figure 2.1.1). Until the middle of the 19th century, dependence on wood for energy was common in most settled parts of the world. Coal is the beginning of the systematic fossil fuel utilization, remained king of the energy world of the 19th century and well into the 20th century.

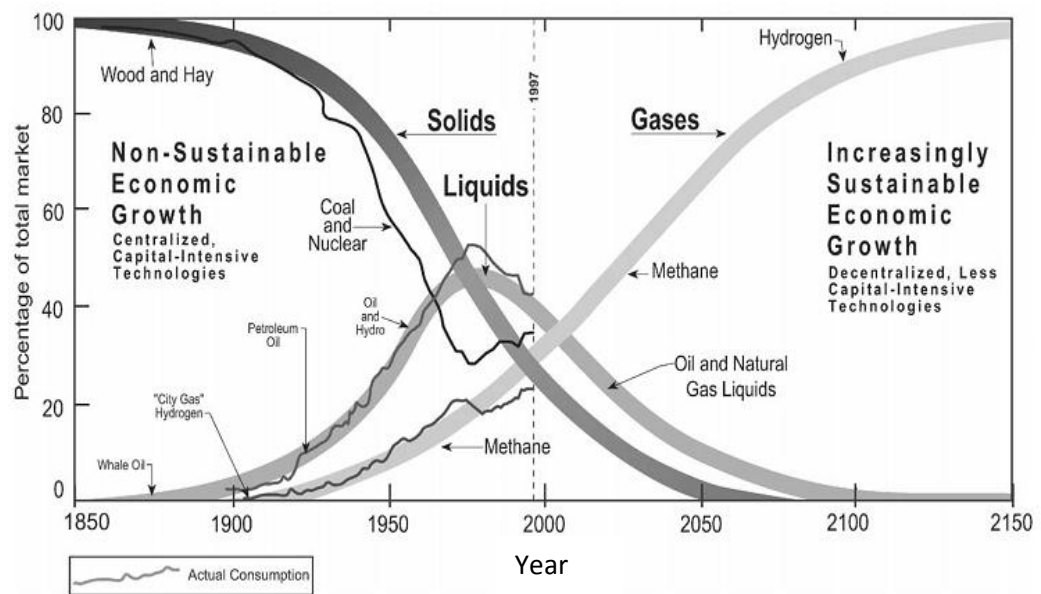


Figure 2.1.1 Global energy systems transition: 1850–2150 (Dunn, 2002).

By 1900 the advantages of an energy system based on fluids, rather than solids, began to emerge as the transportation system started to shift away from railroads and toward automobiles. This shift created problems for coal, with its weight and volume, at the same time that it generated opportunities for oil, which featured a higher energy density and an ability to flow through pipelines and into tanks. By mid-century, oil had become the world's leading energy source (Figure 2.1.1). But dominant as oil is, the liquid now faces an up-and-coming challenger – a gas. Despite improvements from wellhead to gasoline pump, the distribution of oil is rather inconvenient. Natural gas, in addition to being cleaner and lighter and

burning more efficiently, can be distributed through a network of pipes that is less conspicuous, more efficient, and more extensive than the one used for oil. As far as use is concerned, natural gas is now the fastest-growing fossil fuel, the fuel of choice for electricity, and the second-leading energy source, overtaking coal in 1999 (Dunn, 2002).

Status of the Energy in the World has changed significantly in the last years. Energy has become one of the main drivers of economic and social development. Table 2.1.1 shows the actual values for a number of indicators recorded in 1993, the status of these indicators in 2011 and the projections for 2020 made in (World Energy Resources Survey, 2013). Status of the Energy in the World and world reserves in years was shown in the Table 2.1.2. As seen from the Table 2.1.2, energy demand might grow significantly and energy resources and technologies should be available to meet this demand. In this progression, the logical fuel is hydrogen, the lightest and most abundant element in the universe. Today there is a growing interest in the use of hydrogen as fuel. One of the promising hydrogen production approaches is conversion from biomass, which is abundant, clean and renewable.

Table 2.1.1 Key indicators for 1993, 2011 and 2020 (World Energy Resources Survey, 2013)

	1993	2011	2020	Growth % 1993-2011
Population (bilion)	5.5	7.0	8.1	27
Energy Source				
Oil (Mt)	3 179	3 973	4 594	25
Coal (Mt)	4 474	7 520	10 108	68
Natural gas (bcm)	2 176	3 518	4 049	62
Nuclear (TWh)	2 106	2 386	3 761	13
Hydro Power (TWh)	2 286	2 767	3 826	21
Biomass (Mtoe)	1 036	1 277	1 323	23
Other Renewables ((TWh)	44	515	1 999	n/a
Electricity Production/year				
Total (TWh)	12 607	22 202	23 000	76
CO₂ emission/year				
Total CO₂ (Gt)	21	30	42	44

Table 2.1.2 Status of the Energy in the World (Koc, 2013).

Energy Source		World Reserves (2011)	World Reserves in Years	Production (Mtoe)	Consumption (Mtoe)
Crude Oil		225 Mt	52	3995	4059
Natural gas		208 bcm	64	2594	2905
Coal	Hard Coal	404 Mt	112	3955	3724
	Lignite	456 Mt			
Total				10904	10688

Oil is the major source of non-renewable energy in the world and available in abundance in most of the middle east countries including Saudi Arabia, Iran, Iraq while some limited oil wells are present in Venezuela and Canada. Most of the countries still have their dependency on these countries for their oil requirements. This heavy dependence on crude oil (petroleum) makes the issue of its sustainability very important (Kamm et al., 2006). Oil prices are expected to remain high because of the world petroleum demand growing at a fast rate.

Coal is the second source of primary energy in the world after oil and the most abundant form of fossil fuel available on earth. Though coal is still available in big quantity on this earth but it is predicted that will be exhausted in 190 years at current consumption rate (International Energy Outlook, 2005). Coal is classified into four groups; anthracite is the cleanest and slowest burning coal, bituminous coal categorized itself into three: low, medium and high volatile bituminous, sub-bituminous coal is a dull black coal with a calorific value range of 19-27MJ/kg and lignite is a brownish black in color and has generally high ash. Its calorific value is lower than sub-bituminous coal (Valenzuela, 2006). The environmental impact of coal use, especially that coal fired power plants emit gases, especially greenhouse gases, which are the reasons carbon dioxide

emissions, mercury pollution, acid rains and smog, should not be overlooked (Deffeyes, 2005).

Natural gas is a combustible mixture of several gases including methane, ethane, propane and butane. It is the third largest primary energy source in the world and primarily used for generation electricity and heating. Natural gas has significantly low harmful emissions and is one the cleanest form of fossil fuel. Like other fossil fuels, its use emits CO₂ and possibly H₂S depending on the technology used.

Nuclear reactors use Uranium (a finite resource in itself) as a fuel to extract energy from it. The amount of CO₂ emission decreases by utilization of nuclear power plants. As an example, France has decreased its carbon release 50% by producing 80% of total electrical energy as nuclear (Hodgson, 1999). More and more countries are switching to nuclear energy to fulfill their future energy demands. Big problem for the nuclear energy plant is the reactor accidents. So far, there were seven nuclear reactor accidents totally that causes radiation release.

2.1.1 Renewable Energy

With increasing dependence on the fossil fuels, there are many associated environmental effects like land pollution and air pollution which in turn affect both animal and plant life. In the world energy policy, targets to increase current share of renewable energy in coming years, as the fossil fuel become more expensive by reason of its depleting existence. Renewable energy sources include solar energy, hydroelectric power, geothermal, wind and biomass, etc. Total Primary Energy Supply by resource 1993, 2011 and 2013 was shown in the Figure 2.1.1.1.

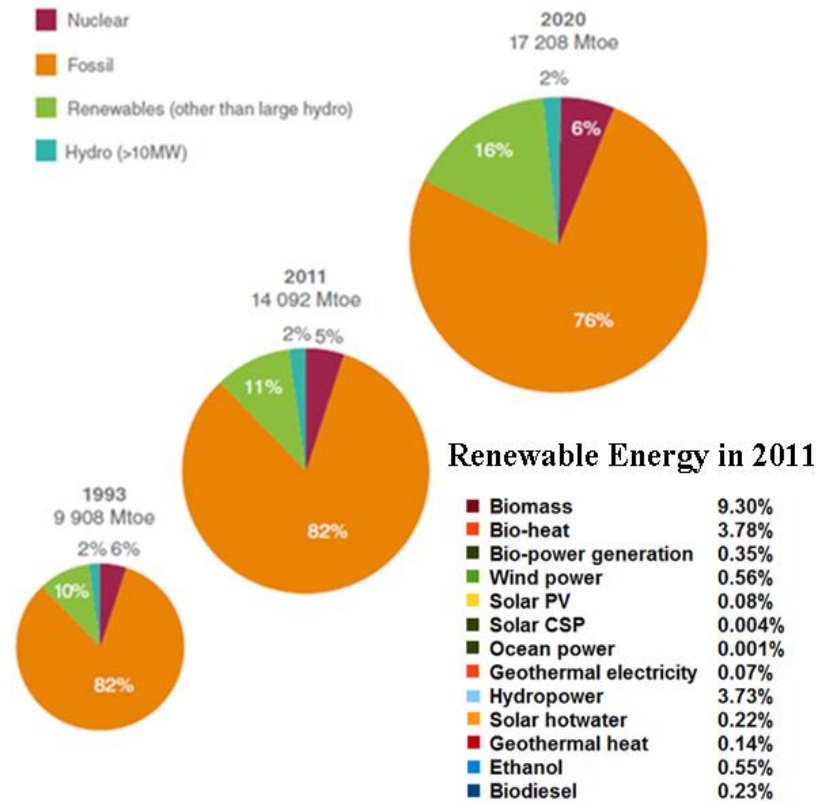


Figure 2.1.1.1 Total Primary Energy Supply by resource 1993, 2011 and 2013. (World Energy Resources Survey, 2013)

Hydroelectric power is not a new technology and provides a significant amount of energy throughout the world. The top 5 largest markets for hydro power in terms of capacity are Brazil, Canada, China, Russia and the United States of America. The global installed hydro power capacity has increased by 8%, but the total electricity produced dropped by 14%, mainly due to water shortages (World Energy Resources Survey, 2013). The main advantage of hydroelectric power generation over petroleum is that hydroelectric power plants use a free source. The disadvantage of this is the fluctuations in flow and water height depending on the climate changes.

Solar energy is the most abundant energy resource and it is available for use in its direct (solar radiation) and indirect (wind, biomass, hydro, etc.) forms. About 60% of the total energy emitted by the sun reaches the Earth's surface. Even if only 0.1% of this energy could be converted at an efficiency of 10%, it would be four times larger than the total world's electricity generating capacity of about 5 000 GW (World Energy Resources Survey, 2013). Main advantages of the solar energy are free, non-polluting and renewable energy. Main disadvantage is that solar energy depends on location and the need for economic energy conversion and storage. Due to the rapidly declining solar panel manufacturing costs, use of solar energy is growing strongly around the world..

Wind energy is available virtually everywhere on earth, although there are wide variations in wind strengths. World wind energy capacity has been doubling about every three and a half years since 1990. Total capacity at the end of 2011 was over 238 GW and annual electricity generation was around 377 TWh, roughly equal to Australia's annual electricity consumption (World Energy Resources Survey, 2013). Positive effects for wind-generated electricity includes; free fuel, no CO₂ emission, leaves no harmful wastes and the land where wind farms are located can be developed as an agricultural land as well (Da Rosa, 2005).

Hydrogen is a commonly used feedstock for the chemical and petroleum industries and a great source of clean energy. Globally, around 45–50 million tonnes of hydrogen are produced each year, the majority of which is produced using fossil fuel feedstocks (Figure 2.1.1.2). Around half is used to produce ammonia, around a quarter is used for hydrocracking in petroleum refining, with the balance used to make methanol and other industrial applications including coal-to-liquids, food processing and electronic industries (Figure 2.1.1.2).

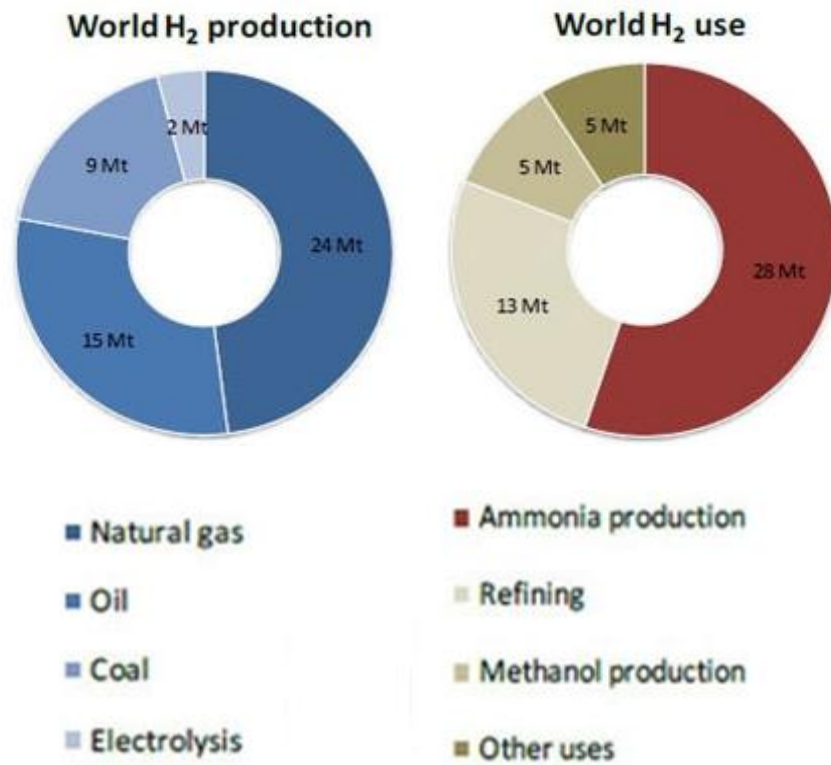


Figure 2.1.1.2 Estimated world hydrogen production and use (Hydrogen Association Evers, 2008).

Hydrogen has the highest energy-to-weight ratio of any fuel since hydrogen is composed solely of the lightest element without heavy carbon atoms appearing in its structure. For a given weight of fuel, the heat liberated from combustion of hydrogen (131 KJ/g) is more than 2.5 times that liberated from combustion of common hydrocarbon fuels, such as gasoline (46 KJ/g) and diesel (Lanz, 2001). Also fuel cells are getting more and more attention from scientific researchers because of their great potential to generate environmental friendly electricity and hydrogen is the basic feedstock to fuel cells.

A fuel cell is a device that converts the chemical potential energy from a fuel into electricity through a chemical reaction with oxygen or another oxidizing agent. There are many types of fuel cells, each with their own unique operating characteristics, but they all consist of an anode, a cathode and an electrolyte that allows charges to move between the two sides of the fuel cell. The anode conducts the electrons that are freed from the hydrogen molecules so that they can be used in an external circuit. It has channels etched into it that disperse the hydrogen gas equally over the surface of the catalyst. The cathode has channels etched into it

that distribute the oxygen to the surface of the catalyst. Electrons are drawn from the anode to the cathode through an external circuit, producing direct current electricity. As the main difference among fuel cell types is the electrolyte, fuel cells are classified by the type of electrolyte they use followed by the difference in startup time ranging from 1 second for proton exchange membrane fuel cells PEM fuel cells, or PEMFC (Figure 2.1.1.3) to 10 minutes for solid oxide fuel cells (SOFC). It also conducts the electrons back from the external circuit to the catalyst, where they can recombine with the hydrogen ions and oxygen to form water. The catalyst is a special material that facilitates the reaction of oxygen and hydrogen. It is usually made of platinum nanoparticles very thinly coated onto carbon paper or cloth. The catalyst is rough and porous so that the maximum surface area of the platinum can be exposed to the hydrogen or oxygen.

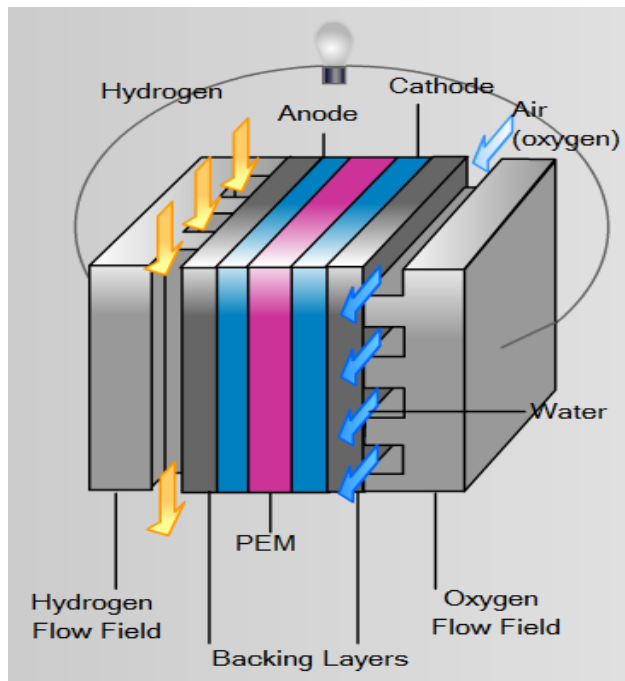


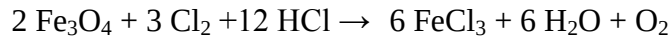
Figure 2.1.1.3 A Schematic presentation of (PEM) fuel cell.

Due to the many advantages and using areas of hydrogen as a fuel, many research groups have tried to produce hydrogen. Although hydrogen is an abundant element, it does not occur naturally and is normally bonded with organic compounds, so that hydrogen must be produced from hydrogen containing compounds. There are various conventional technologies for hydrogen production including electrolysis of water, classical gasification of fossil fuels, steam reforming of light hydrocarbons and photolytic processes. Electrolysis of water

has been a traditional way to produce hydrogen energy (Turner, 2004). In this way electricity is consumed to decompose water directly into its components of oxygen and hydrogen. Due to the high cost of electric energy, this process is practical only where electricity can be economically generated from nuclear, solar energy, or hydropower. Photolytic processes are another viable option if the efficiency of this technology can be improved to support the economic costs (Behnia, 2013). Nevertheless this technique is still used in the high purity of hydrogen required processes like hydrogenation of unsaturated fats and vegetable oil. Another possible way for hydrogen production is that traditional gasification of fossil fuels but they are limited to only low water content feedstocks (Elliott, 2008). Hydrogen can also be produced through gasification of coal. Solid coals are pulverized and then partially oxidized with steam and oxygen. The product gas contains CO, CO₂, H₂, H₂O and H₂S, which is removed in purification. The gas mixture is quenched by water to remove ash particles, then fed to a shift reactor to further convert CO to CO₂ and produce additional H₂. The effluent gas is purified through a pressure swing adsorption or scrubbing process to obtain high purity hydrogen. Hydrogen production via coal gasification is the least economic among the processes, because it needs a gasification plant which requires a huge investment and the energy efficiency in this process is very low. The catalytic steam reforming of natural gas is the most economical process for producing hydrogen because it has the highest thermal efficiency and lowest capital investment.

All of these techniques are dependent on the fossil fuels which have limited reservations, so that they are not desirable to produce hydrogen in a convenient way. As mentioned before in the Figure 2.1.1 today there is a growing interest in the use of hydrogen as fuel instead of fossil fuels. Because of these reasons new techniques have to be developed to produce hydrogen energy from non-fossil energy sources. Researchers are developing advanced processes to produce hydrogen from sustainable resources economically. Clean biomass and biomass-derived precursors such as ethanol and sugars are appropriate precursors for producing hydrogen through different conversion strategies. The second option explored here is hydrogen production from water splitting by means of the photons in the visible spectrum. Another potential way to produce hydrogen is

biogenic production. Some types of algae and bacteria, when exposed to sunlight, will give off hydrogen. Also many research groups investigated hydrogen production by inorganic reactions. Polat et al. classified these inorganic reactions according to step numbers (Polat et al., 2012). For example, hydrogen production over FeCl_2 (Weissermehl et al., 1978);



As the dependence on fossil fuels in the world increases and due to the environmental considerations, i.e. increasing atmospheric toxic gases (CO_2 , SO_2 , NO_x and other pollutants) concentrations from the combustion of fossil fuels, researches of alternative energy sources are getting more attention. Biomass as a renewable and alternative energy source has a great potential to supply of the worlds increasing energy demand. Biomass is readily available, only carbon based material in renewable energy groups and also carbon-neutral feedstock can be converted into fuels and chemicals. Wastes and residues are used by biomass energy technologies, this reducing waste disposal problems and making better use of resources.

2.2 Status of the Energy in Turkey

Turkey has quite diverse energy resources, including hard coal, lignite, hydropower, geothermal, solar, natural gas, oil, wood, animals and plants wastes. Energy outlook of Turkey was given in the Table 2.2.1. However, utilization of these resources is not at desired levels to meet the demand of the Turkey. Since Turkey is a socially and economically developing country, the energy demand of Turkey has been growing more rapidly than the energy production. Turkey's total primary energy production and consumption during 1990 and 2011 was shown in the Figure 2.2.1. Also natural gas and electricity prices have been increasing day by day in Turkey, because of the dependency on energy imports, primarily of oil and gas. The share of energy sources used for electricity production in 2011 was shown in the Figure 2.2.2. Thus, the renewable energy sources have become a challenging alternative to fossil fuels for the country.

Table 2.2.1 Energy outlook of Turkey (Mavi Kitap, 2011).

Energy Resources	Proved	Probable	Possible	Total
Hard Coal (Mt)	534.6	431.5	368.4	1.134.6
Lignite (Mt)				
Elbistan	4.917,9			4.917,9
Other	4.920,0	1.345,0	262,0	6.527,0
Total	9.837,9	1,345,0	262,0	11.444,9
Asphaltite (Mt)	40,7	29,5	7,3	77,5
Bituminous (Mt)	1.641,4			1.641,4
Hydraulic (GWh/year)	129.388			129.388
Crude Oil (Mt)	44.3			44.3
Natural Gas (bcm)	6.2			6.2
Nuclear (t)				
Uranium	9.129			9.129
Thorium	380.000			380.000
Geothermal (MW/year)				
Electricity	98		512	600
Heat	3.348		28.152	31.500
Solar (Mtoe)				
Heat				32,6
Wind				
Electricity (MW)				48.000
Biomass (Mtoe)				
Electricity				2,6
Heat				6,0

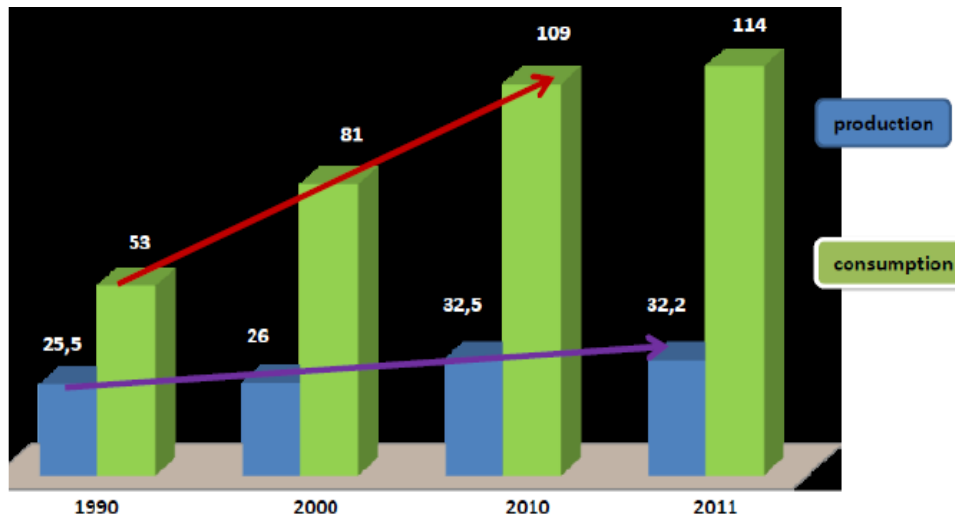


Figure 2.2.1. Turkey's total primary energy production and consumption during 1990 and 2011 (Mtoe) (Turkyilmaz, 2013).

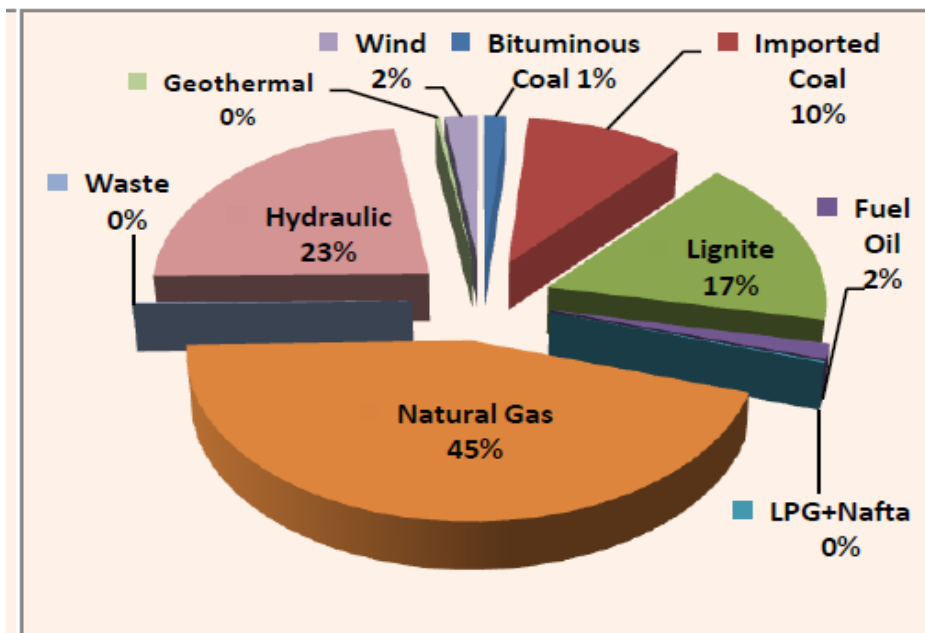


Figure 2.2.2 The share of energy sources used for electricity production in Turkey-2011 (World energy council, 2012).

In 2012 the Turkish coal sector produces hard coal (2.3 million tonnes) and lignite (70.0 million tonnes), mainly used for power generation. At present only a small power station (300 MW) is fed with domestic hard coal from the Zonguldak basin, whilst the larger İskenderun power plant (1 200 MW) and Zonguldak Eren Enerji Çatalağzı power plant (1 360 MW) use imported hard coal. Other power plants use lignite. In total, Turkish coal - fired plants have a capacity of approximately 12.2 GW (Eurocoal, 2010).

Turkey is a country which has the highest hydropower, wind and geothermal energy potential among European countries. Turkey aims at fully utilizing its renewable resources such as hydroenergy, wind and solar energy to meet the demand growth in a sustainable manner. According to the multi-criteria analysis tool developed in the Environmental Impact Assessment (EIA) report to evaluate the renewable energy source (RES) technologies, the most appropriate renewable energy alternative for Turkey is biomass (Baris et al., 2012). Economically feasible hydropower potential of Turkey's major river basins in 2006, average solar energy potential of Turkey and insolation durations on monthly basis, technical wind energy potential by regions in Turkey were given in the Tables 2.2.2, 2.2.3 and 2.2.4, respectively.

Table 2.2.2 Economically feasible hydropower potential of Turkey's major river basins in 2006 (Barış et al., 2012).

River basin	Energy Potential (GWh/year)	Power Potential (MW)	Runoff (Tm³/year)
Euphrates	37,8	9555	33.5
Tigris	16,6	4890	21.8
East Black Sea	13,2	3900	14
Coruh	10,9	3247	6,5
Seyhan	6957	1788	7.06
East Mediterranean	6749	1856	12.27
Kızılırmak	6420	2116	6.28
Ceyhan	5996	1779	7.21
Antalya	5345	1437	7.76
Yeşilirmak	4984	1257	5.54
West Mediterranean	3240	881	11.24
Sakarya	2585	1191	6.03
West Black Sea	2149	642	10.04
Aras	2692	868	5.54
Total	125,699	35.407	155

Table 2.2.3 Average solar energy potential of Turkey and insolation durations on monthly basis (EIE, 2010).

Months	Total monthly solar energy (kWh/m²-month)	Insolation duration (h/month)
January	51.7	103
February	63.3	115
March	96.7	165
April	122.2	197
May	153.9	273
June	168.8	325
July	175.4	365
August	158.4	343
September	123.3	280
October	89.9	214
November	60.8	157
December	46.9	103
Total	1311	2640
Average	3.6 (kWh/m ² -day)	7.2 h/day

Table 2.2.4 Technical wind energy potential by regions in Turkey (EIE, 2009).

Region	Wind (MW)	Power	Potential	Percentage
Marmara	43,9			38.5
Aegean	26,2			22.9
Black Sea	14,3			12.5
Mediterranean	11,2			9.8
Central Anatolia	10,9			9.6
South- eastern Anatolia	4703			4.1
Eastern Anatolia	2974			2.6

The annual biomass energy potential of Turkey is estimated as 32 Mtoe as shown in the Table 2.2.5. The recoverable biomass energy potential come from; agricultural residues, farming wastes, forestry and wood processing residues, animal wastes and municipal wastes. The largest energy potential portion of this product is used in rural areas for heating and cooking in a primitive way. Turkey is a country which has rich agricultural potential arising out of its ecological conditions with 23.07 million ha agricultural arable land. So that Turkey is one of the important countries in terms of agricultural production. 18.11 million ha is cultivated and remaining part (5.59 million ha) is fallowing land. Total annual agricultural potential in Turkey was given in the Table 2.2.6. Total amount of agricultural solid waste in Turkey is 40-55 million tones and Energy potential is around 15.5 Mtoe (Saraçoğlu, 2007).

Table 2.2.5 Total annual and Energy potential in Turkey (Olgun, 2013).

Biomass	Annual potential (Mtons)	Energy (Mtoe)
Annual crops	54.4	15.5
Perennial crops	16.0	4.1
Forest residues	18.0	5.4
Residues from agro-industry	10.0	3.0
Residues from wood industry	6.0	1.8
Animal wastes	7.0	1.5
Other (municipal)	5.0	1.3
Total	116.4	32.6

Table 2.2.6 Total annual agricultural potential in Turkey (Saraçoğlu, 2007).

Annual Crops	Annual Production (Mtons)	Energy Potential (Mtoe)
Wheat straw	26.4	7.2
Barley straw	13.5	3.9
Malze stalk	4.2	1.2
Cotton cocoon shell	2.9	0.9
Sunflower shell	2.7	0.8
Sugar beet waste	2.3	0.7
Hazelnut shell	0.8	0.3
Oat straw	0.5	0.2
Rye straw	0.4	0.1
Rise husk	0.4	0.1
Fruit shell	0.3	0.1
Olive cake	0.75	0.3
Total	54.4	15.5

2.3 CHEMICAL COMPOSITION OF BIOMASS

Biomass is mainly composed of cellulose, hemicellulose, lignin, and extractives and the compositions vary depending on the source of the biomass. These major structural components generally have rough compositions of 30-50% of cellulose, 20-40% of hemicelluloses, 15-25% of lignin and 1-3% extractives. The composition of these constituents can vary from one plant species to another. For example, the extractive ratio can be increased to 40-50% for some biomass species. In addition, the ratios between various constituents within a single plant vary with age, stage of growth, and other conditions.

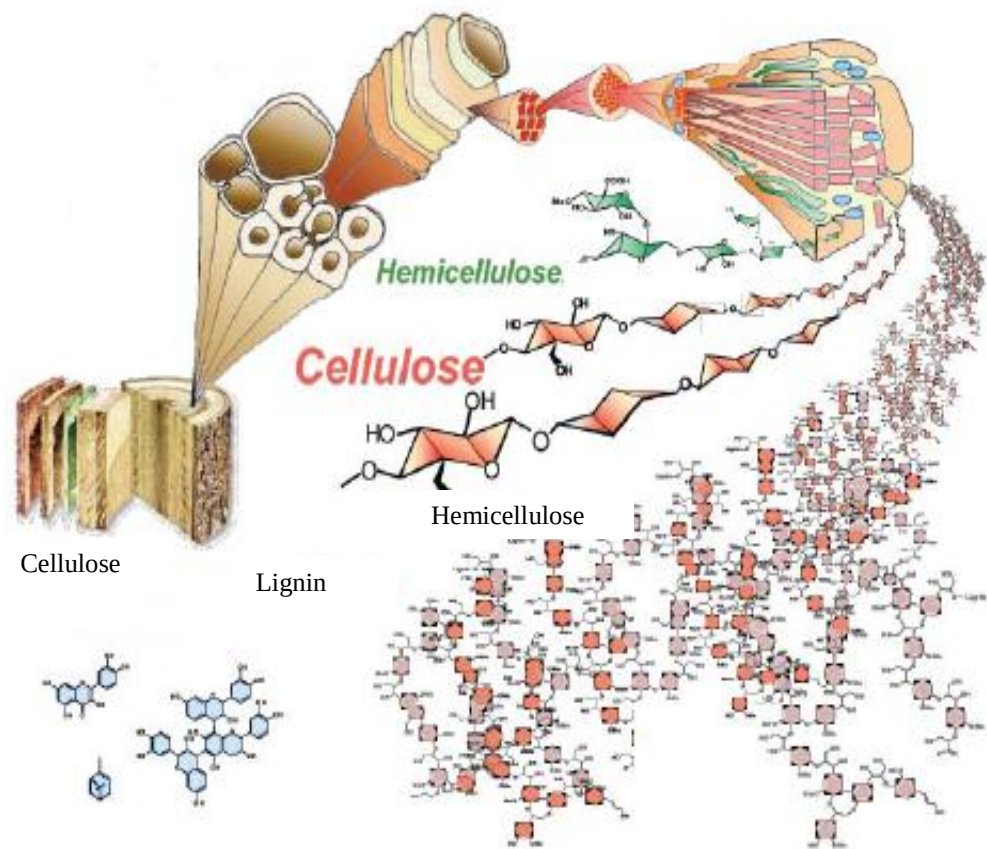


Figure 2.3.1 Schematic presentation of the biomass major components (Dahmen et al., 2010).

Figure 2.3.1 shows a schematic presentation of the major components. Cellulose is a major structural component of plant cell walls, which is responsible for mechanical strength, while hemicellulose macromolecules consist of often repeating polymers of pentoses and hexoses. Hemicellulose has a lower molecular

weight than cellulose and its role is to connect lignin and cellulose fibers. Lignin is generally the most complex and smallest fraction. It holds together cellulose and hemicellulose fibers and forms a protective seal around these components to give support, resistance and impermeability to the plant (Figure 2.3.2).

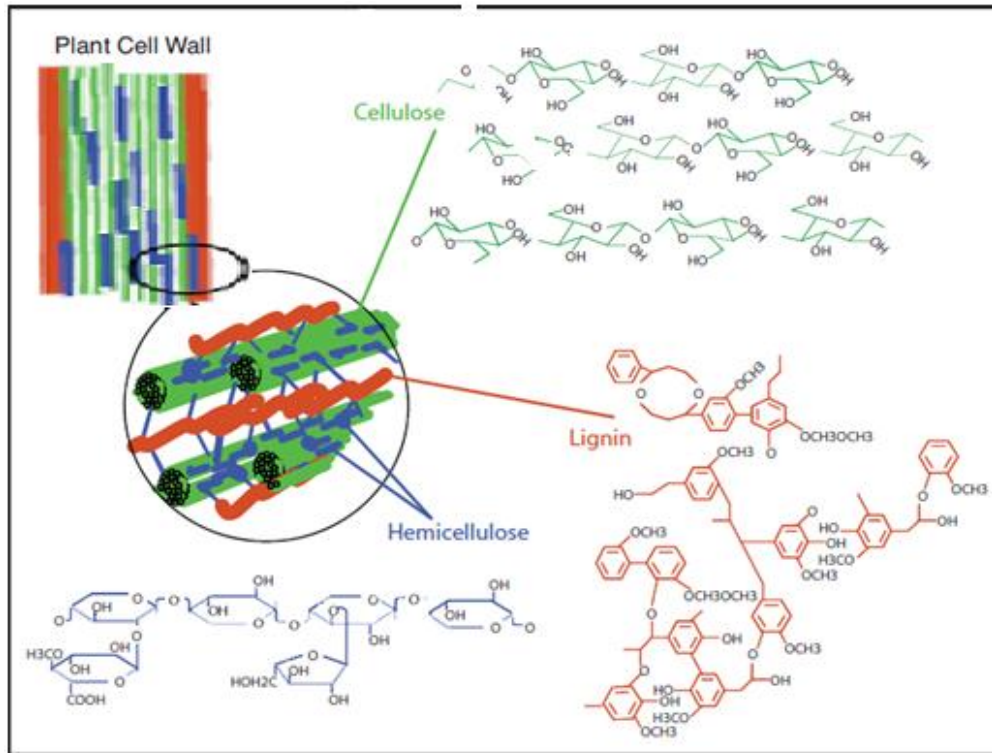


Figure 2.3.2 Schematic presentation of the plant cell wall.

Typical compositions of different biomass species were given in the Table 2.3.1. Typical compositions of different biomass species, analyzed in the TUBITAK Projects 106T678 and 109M284, were given in the Table 2.3.2. The components that are present generally in lignocellulosic biomass can be classified in idealized outline in the Figure 2.3.3. Macromolecular substances are the major portion of the biomass and composed of polysaccharides and lignin. The polysaccharides include cellulose and hemicellulose. Low-molecular weight substances are categorized into two groups; organic and inorganic matters. Extractives are soluble in organic solvents and in cold or hot water, or are volatile with steam.

Table 2.3.1 Typical compositions of different biomass species (%) (Vigouroux, 2001).

	Cellulose	Hemi-cellulose	Lignin	Extractives	Ash
Softwood (average)	45.8	24.4	28.0	n.a	1.7
Hardwood (average)	45.2	31.3	21.7	n.a	2.7
Wood bark	24.8	29.8	43.8	n.a	1.6
Bagasse	41.3	22.6	18.3	13.7	2.9
Coconut shell	36.3	25.1	28.7	8.3	07
Corn stalks	42.7	23.6	17.5	9.8	6.8
Olive husk	24.0	23.6	48.4	n.a	4.0
Wheat straw	30.5	28.9	16.4	2.4	6.6-11.2
Rice husk	31.3	24.3	14.3	8.4	23.5
Rice straw	37.0	22.7	2.6	2.1	16-19

Table 2.3.2 Typical compositions of different biomass species (% daf) and ash content (Sağlam 2010 and 2013).

	Cellulose	Hemi-cellulose	Lignin	Extractives	Ash
Leek	30.8	7.9	4.3	56.1	13.2
Cabbage	29.8	7.7	4.5	57.2	12.4
Almond	43.1	23.3	28.8	4.4	0.9
Walnut	42.4	16.3	35.4	5.4	1.0
Hazelnut	38.2	12.1	40.0	8.6	1.7
Acorn	24.8	16.5	12.1	45.1	2.5
Corn stalk	33.0	33.6	4.2	29.2	8.2
Corn cob	31.5	41.2	4.4	22.3	2.9
Cotton stalk	50.5	11.7	19.4	16.9	6.9
Tobacco stalk	49.8	16.4	13.4	19.2	11.7
Sunflower stalk	54.5	9.7	13.9	21.5	13.1
Poplar sawdust	55.8	14.9	20.2	7.08	2.6
Pine sawdust	39.8	11.4	32.4	15.8	2.3
Fir sawdust	45.2	9.8	35.1	7.9	2.2

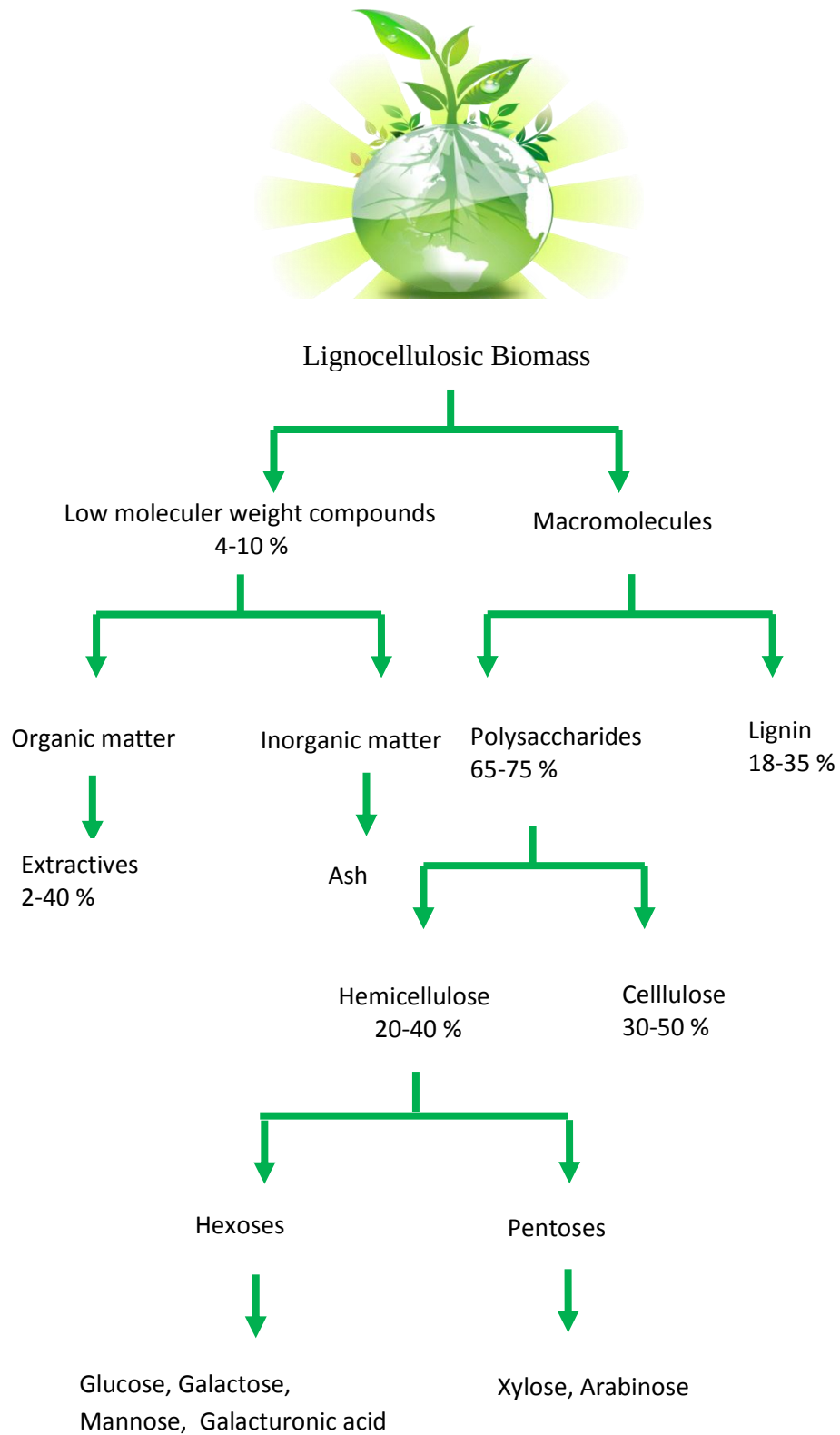


Figure 2.3.3 Composition of lignocellulosic biomass (adapted from Ramsurn, 2013)

2.3.1 Cellulose

Cellulose is one of the naturally polymer in the world, and the basic building block for many textiles and for paper. The existence of cellulose as the common material of plant cell walls was first recognized by Anselm Payen in 1838, who realized that the cell wall of plants is not one uniform chemical substance (Browning, 1963). Cellulose is a homopolysachharide consisting of a linear chain repeating units of cellobiose-a dimer of β -D-glucose. They are connected via bonds, which have strong intra-and intermolecular hydrogen bonds. These strong bonds make cellulose structure crystalline and resistant to swelling in water and does not melt or dissolve in common solvents. In hydrothermal conditions water can break up the crystalline structure and hydrolyze bonds and so that glucose monomers can be produced. Structure representation of cellulose is shown in Figure 2.3.1.1.

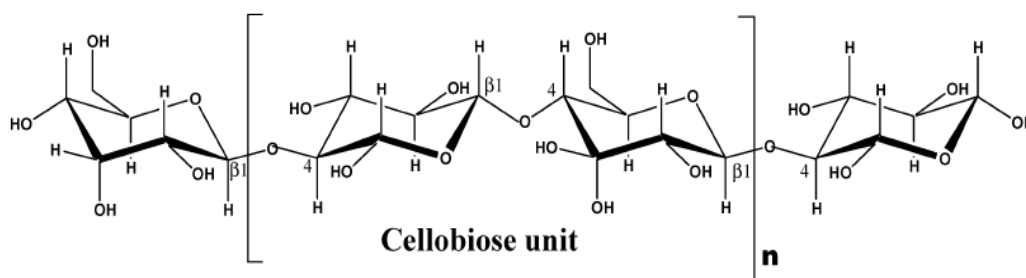


Figure 2.3.1.1 Structure representation of cellulose.

The primary occurrence of cellulose is the existing lignocellulosic material in forests. Other cellulose-containing materials include agriculture residues, grasses, water plants, and other plant substances. Commercial cellulose production concentrates on naturally highly pure sources such as cotton. Cellulose hydrolysis is favored generally above 210-220°C. For example, in order to reach approximately 50% glucose conversions from cellulose, relatively high acid concentrations (1%) and temperatures (220-240°C) are obligatory (Bobleter, 1994).

2.3.2 Hemicellulose and Pectin

In contrast to cellulose, which is a homopolysaccharide, hemicelluloses are heteropolysaccharides and also not chemically homogeneous (Saha, 2003). In the Table 2.3.2.1, a comparison table of the cellulose and hemicellulose was given. Hemicellulose is chained and amorphous biopolymer composed of the primary monomer constituent hexoses (glucose, galactose and mannose), pentoses (xylose, arabinose), glucuronic acid and galacturonic acid with a low polymerization degree of 50-300 (Pacheco, 2009). Main components of hemicelluloses were shown in the Figure 2.3.2.1. A sample for the chemical structure of hemicellulose was given in the Figure 2.3.2.2. Hemicellulose compositions of different biomass species, analyzed in the TUBITAK Projects 106T678 and 109M284, were given in the Table 2.3.2.2.

Within the plant, these monomers which are forming homopolymer (xylan, arabinan, mannan, galactan, etc.,) or copolymer (glucomannan, arabinogalactan, galactoglucomannan etc., Figure 2.3.2.3) structures are linked to lignin or cellulose by chemical bonds. The branching in hemicelluloses causes them to be more accessible and thus more susceptible to the action of solvents and chemical reactions. For example, Garrote et al. (1999) noted that for hydrothermal treatments, hemicelluloses were best hydrolyzed within the range of 150 – 230°C. Beginning at approximately 180°C, the hemicelluloses is easily dissolved in water (Bobleter, 1994). For example, approximately 40% of the poplar wood, wheat straw, birch wood and rice straw are dissolved by the hot water at 190°C, and 230°C ca 60 % (Bobleter, 1994).

Table 2.3.2.1 Comparison of the cellulose and hemicelluloses properties (Wang, 2003).

	Cellulose	Hemicellulose
Monomer	Pure glucose	Mixed sugars
Polymer chain length	Long (5 μ m)	Short
MW	High (1000 units)	Low (100 units)
Polymer topology	Linear	Branched
Side groups substitution	No substitution	On C ₂ , C ₃ and C ₆
Polymer morphology	Crystalline+amorphous	Amorphous
Solubility	Low	High
Reactivity	Less reactive	More reactive
Hydrolysis	Partial	Readily (susceptible)

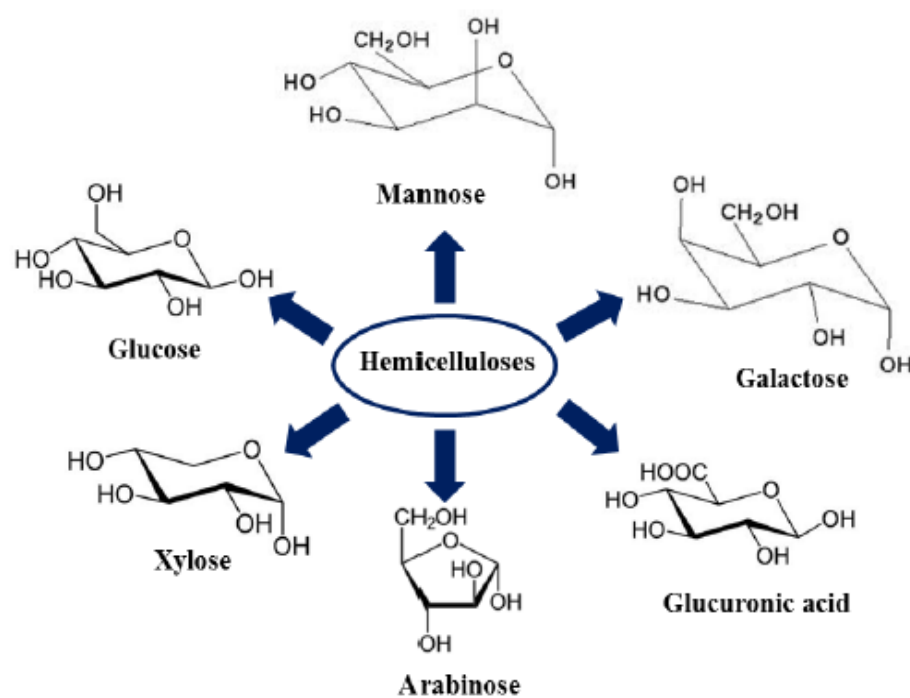


Figure 2.3.2.1 Main components of hemicellulose (Ramsurn, 2013).

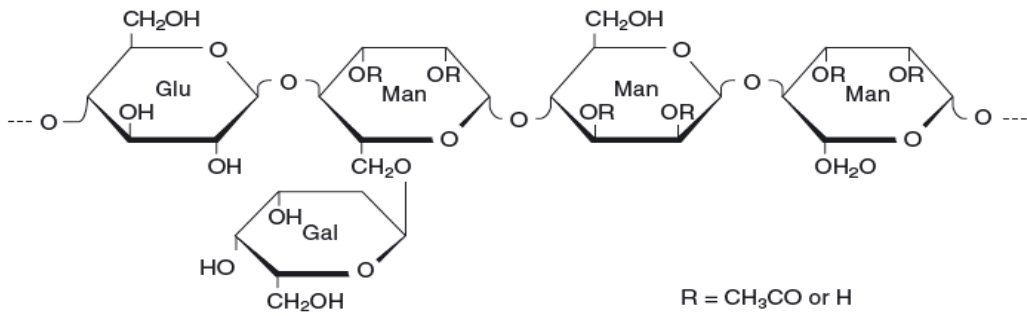


Figure 2.3.2.2 Chemical structure of hemicelluloses (Zhang, 2010).

Table 2.3.2.2 Hemicellulose compositions of different biomass species (% daf), (Sağlam 2010 and 2013).

	Glucose	Mannose	Galactose	Xylose	Arabinose
Leek	34.2	0.9	0.5	1.5	1.2
Cabbage	35.7	0.7	0.6	1.8	1.1
Almond	50.4	0.4	2.8	13.0	1.3
Walnut	51.9	0.5	0.9	8.9	0.6
Hazelnut	45.3	0.6	1.2	5.1	1.7
Acorn	30.5	1.4	2.1	6.6	2.2
Corn stalk	42.5	2.1	3.1	18.2	3.7
Corn cob	39.9	3.3	4.5	19.9	4.2
Cotton stalk	56.7	0.9	1.6	5.8	1.1
Tobacco stalk	57.6	1.7	2.0	8.2	0.9
Sunflower stalk	56.2	0.5	1.4	4.9	1.2
Poplar sawdust	65.3	1.5	0.2	8.1	0.7
Pine sawdust	48.2	3.0	0.6	2.4	1.2
Fir sawdust	52.2	3.4	0.1	2.8	1.3

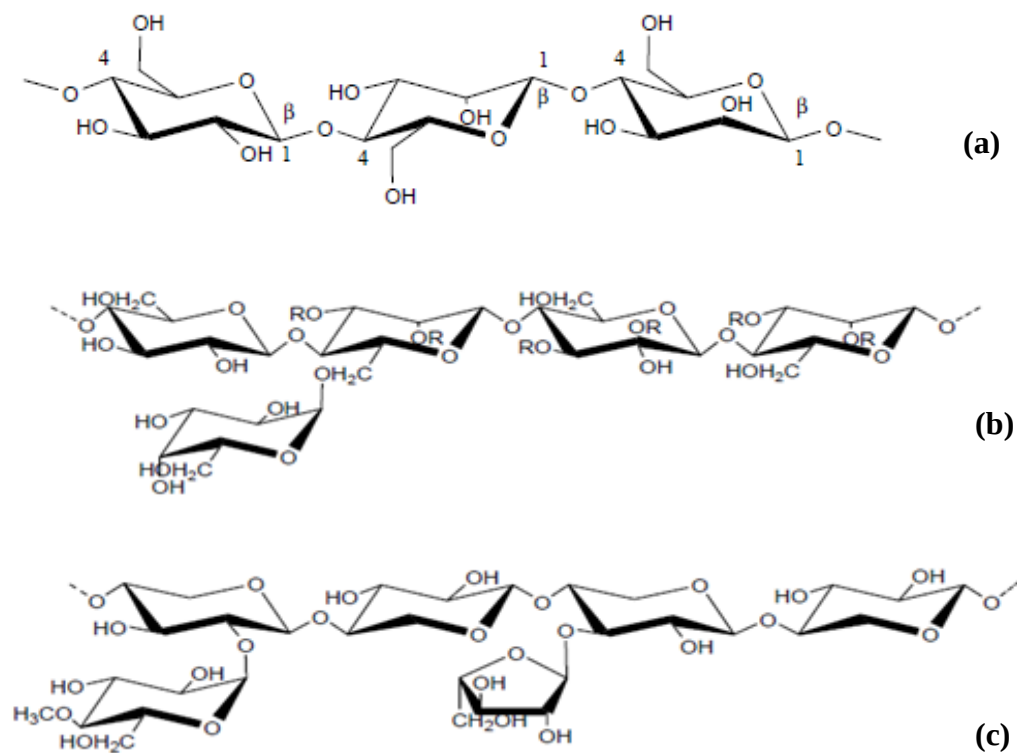


Figure 2.3.2.3 Hemicelluloses. (a) Glucomannan, (b) Galactoglucomannan; (c) Arabinoglucuronoxylans.

Table 2.3.2.3 Major Hemicellulose Components (Wang, 2003).

Wood Type	Hemicellulose Type	Amount (% of wood)
Softwood	Galactoglucomannan	5-8
Softwood	(Galacto)glucomannan	10-15
Softwood	Arabinoglucuronoxylan	7-10
Larch wood	Arabinogalactan	5-35
Hard wood	Glucuronoxylan	15-30
Hard wood	Glucomannan	2-5

Table 2.3.2.3 shows the hemicellulose components in various wood types that vary in composition due to the genetic variability among different sources. Also for the same type wood, this ratio can be changed by the age of wood or by the climate conditions. For example in coniferous wood (softwood), the major hemicelluloses are galactoglucomannan, glucomannan and arabinoglucuronoxylan. Other softwood hemicelluloses are arabinogalactan, xyloglucan and other glucans. Other polysaccharides are pectins. The term pectin or pectic compounds is used either strictly for the component rhamnogalacturonan or more generally for the group of components comprising rhamnogalacturonans, galactans and arabinans (Laine, 2005). Linear structure of pectin is given in the Figure 2.3.2.4. Pectin is a polysaccharide made mostly of galacturonic acid units. The galacturonic acids are frequently esterified with a methyl group. According to esterification ratio, pectins are named as low methoxyl and high methoxyl pectins. Pectin is used extensively in the food industry as a gelling agent. Not only is it used in jams and jellies, but also as a thickening agent and protein stabilizer. It is also added to diet sodas to improve mouthfeel.

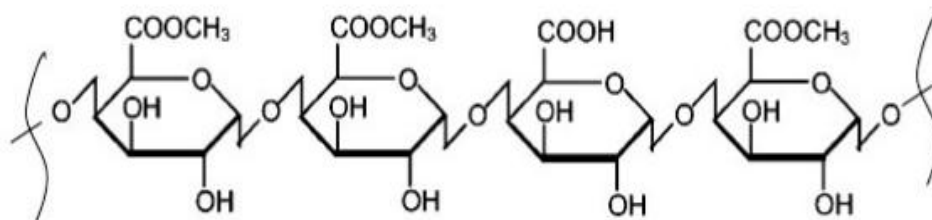


Figure 2.3.2.4. Structure of Pectin molecules.

In hardwoods, xylan is a hetero-polysaccharide that consists of a homopolymeric backbone of β -(1,4) linked to xylose residues, which is generally the most common structure in hemicellulose. Most of the hydroxyl groups at C2 and/or C3 of the xylose units are substituted with acetyl groups. Unlike softwood xylan, hardwood xylan does not contain arabinose side chains (Laine, 2005). Hardwood also contains glucomannan with a backbone of β -(1-4)-linked D-mannopyranose and D-glucopyranose units (Fengel et al. 1989, Sjöström 1981).

2.3.3 Lignin

Lignin is described as a random, three-dimensional network polymer comprised of variously linked phenylpropane units (Sjöström, 1981). Lignin is a complex high molecular weight compound with three most prevalent monomers as p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol proportions vary depending on the type of biomass (Figure 2.3.3.1). The main precursor of lignin in softwoods is trans-coniferyl alcohol. In hardwoods, trans-sinapyl alcohol and trans-p-coumaryl alcohol are also lignin precursors. The precursors are polymerized during lignin biosynthesis. Proposed structural segment of softwood lignin was shown in the Figure 2.3.3.2. Lignin degradation is probably achieved at temperatures below 200°C. Hydrothermal treatment of hardwoods renders approximately 50% of the lignin in solution even at 200°C. At 365°C, over 90% of the lignin can be dissolved after a hydrothermal reaction time of only 0.4 min (Bobleter, 1994).

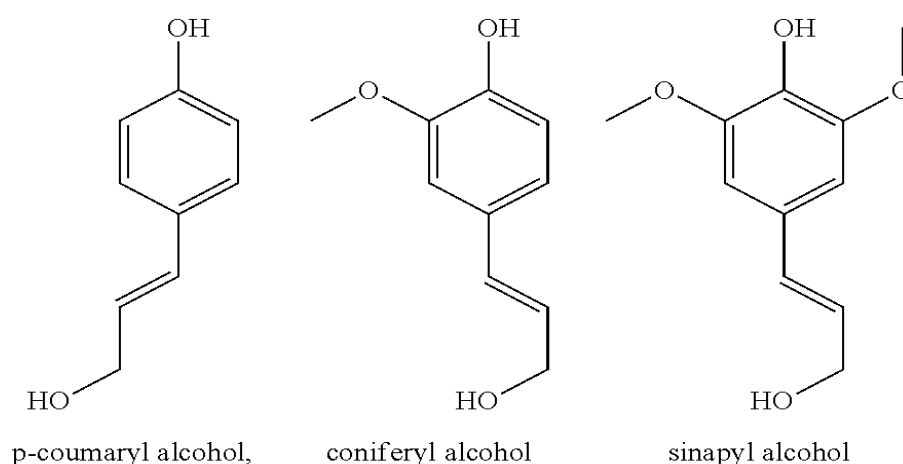


Figure 2.3.3.1 Main building blocks of lignin.

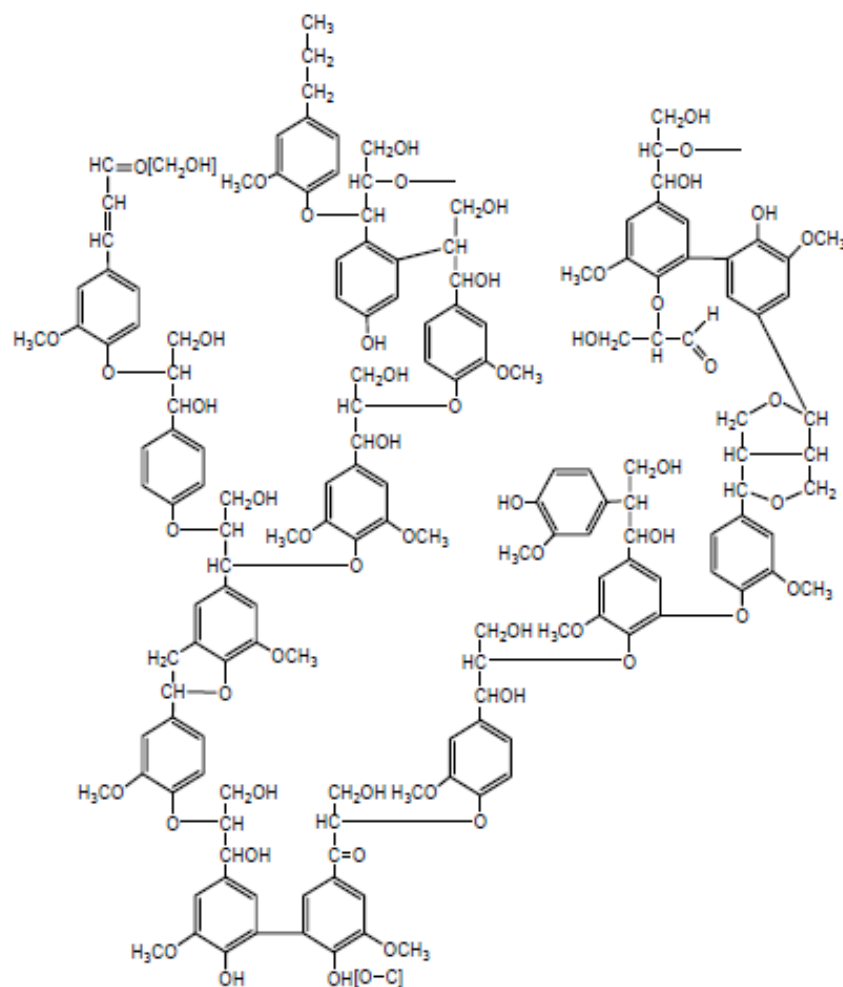


Figure 2.3.3.2 Proposed structural segment of softwood lignin (Sjöström, 1981).

Lignin polymerization is initiated by oxidation of the phenylpropane phenolic hydroxyl groups. Freudenberg has shown that lignin precursors undergo dimerization through enzymatic dehydrogenation, which is initiated by an electron transfer and yields resonance-stabilized phenoxy radicals (Freudenberg, 1968). Stabilization of the radical occurs by coupling to another radical in any of the positions of the unpaired electron.

2.3.4 Extractives

All species of wood and plants contain small amounts of substances in addition to cellulose, hemicelluloses and lignin. To distinguish them from the major cell wall components these additional constituents are known as the extraneous components (Browning, 1963). They are typically in the order of 2-40% of dry wood weight, depending on species and, location in the tree. The extractives often play an important role in the utilization of wood, and influence the physical properties of the wood (Roth et al., 1960). Aliphatic and aromatic hydrocarbons, volatile oils, fatty acids, waxes, terpenes, aliphatic and aromatic acids and their salts, alcohols, phenols and phenolic constituents such as stilbenes, lignans, tannins and flavonoids, aldehydes, ketones and quinines, esters and ethers comprise the wood extractives. Certain wood and plant contain appreciable amounts of water-soluble polysaccharides; others contain cyclitols. All types of plants contain very small amounts of proteins (Wise 1952, Browning 1963). Volatile oils are responsible for the characteristic odors associated with the freshness. Fatty acids are the common unsaturated C₁₈ acids, with one, two, and three double bonds, respectively. Oleic, linoleic, palmitic acids are the most abundant fatty acids. The phenolics have fungicidal properties and affect natural wood color. Fats and waxes, as in other biological systems are utilized as energy source while terpenoids and steroids are what are known as oleoresins. Some extractives are pharmaceutically important. For example, flavanoids are used as antioxidants and as antivirals (Sharma 2006, Balasundram et al. 2006, Brahmachari et al. 2006).

One of the most important commercial applications for wood extractives is the use of tannins in leather manufacture. The tannins are responsible for the conversion of animal skins into leather. The vegetable tannins are comprised of substances with a high proportion of free phenolic hydroxyl groups and of varying degrees of condensation or polymerization (Browning, 1963). Schematic presentation of molecular structure of tannin was shown in the Figure 2.3.4.1. Tannins can be divided into the hydrolyzable class, the condensed tannins and phlorotannins (Figure 2.3.4.2). Gallic acid, ellagic acid, and glucose are common hydrolysis products. The condensed tannins on treatment with acid are polymerized further, rather than being hydrolyzed into simpler substances (Browning, 1963). Gallic acid and glucose are obtained by the hydrolysis of tannic acid with 5% sulfuric acid around 100°C. When heated above 220°C, gallic acid loses carbon dioxide to form pyrogallol or 1,2,3-trihydroxybenzene (Figure 2.3.4.3). The tannic acid or tannin is already present in woods like oak, walnut, chestnut tree, mahogany and sumac. Generally chestnut tree contains 9 % tannin, oak 30 % and sumac 25-27% (Table 2.3.4.1).

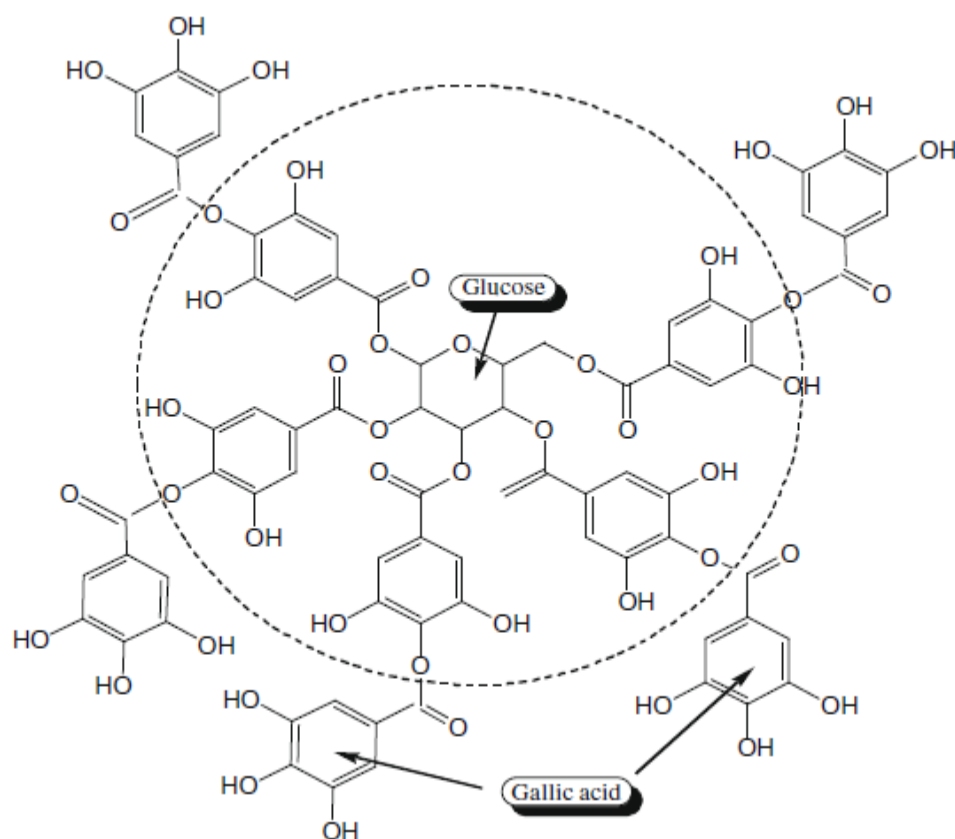
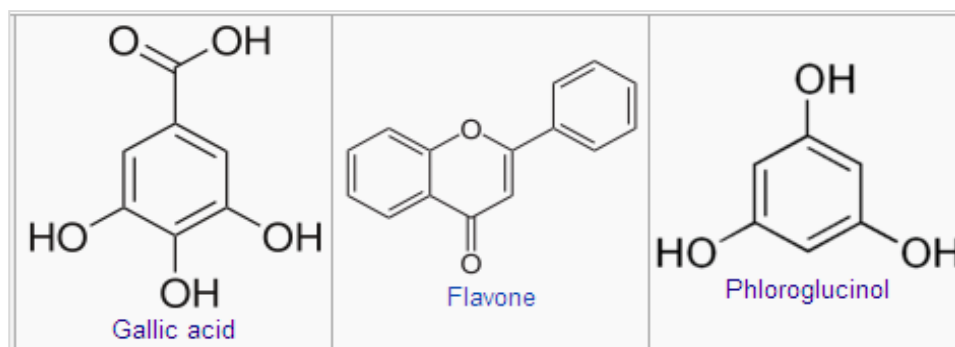


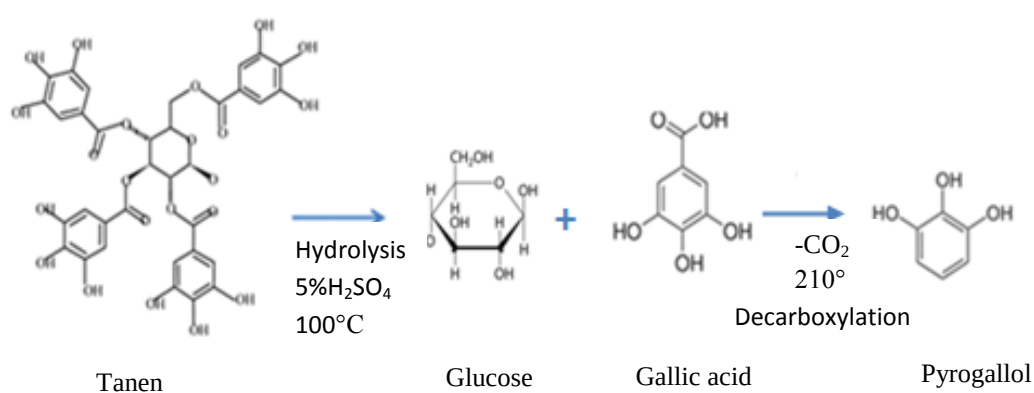
Figure 2.3.4.1 Schematic presentation of tannin.



a) Hydrolyzable tannins

b) Non-Hydrolyzable
or condensed tannins

c) Phlorotannins

Figure 2.3.4.2 Classification of tannin.**Figure 2.3.4.3** Schematic presentation of pyrogallol formation.**Table 2.3.4.1** Tannin percentages in some selected plants

Name of the Plant	Tannin (%)
Bruguiera	17-36
Oak	30
Xylocarpus	24
Sumac	25-27
Eucalyptus	4-20
Chestnut tree	9
Chestnut	75
Valonia	47

2.3.5 Ash

Minerals are necessary for plant growth and the composition of the mineral matter depends on the environmental conditions. The mineral constituents are composed of salts of calcium, potassium, and magnesium. The acid radicals are carbonates, phosphates, silicates, sulfates and oxalates. Generally plants contain less than 1 % of ash, some tropical plants contain 4 to 5 % (Browning, 1963).

2.4 Biomass Conversion Technologies

Biomass is considered the renewable energy source with the highest potential to contribute to the energy needs of modern society for both developed and developing world-wide economies. The biomass energy resource has many advantages such as lower price, less sulphur composition, less ash content and the feature of renewability. Also biomass is formed by fixing carbon dioxide in the atmosphere during the process of plant photosynthesis, biomass can lead to zero CO₂ emission in lifecycle. Biomass resources include primary, secondary, and tertiary sources of biomass. Primary biomass resources are produced directly by photosynthesis and are taken directly from the land. They include woody crops and herbaceous crops, the seeds of oil crops, and residues resulting from the harvesting of agricultural crops and forest trees. Secondary biomass resources result from the processing of primary biomass resources either physically, chemically or biologically. Tertiary biomass resources are post-consumer residue streams.

There is increasing recognition that low-cost, high-capacity processes for the conversion of biomass for replacing fossil fuels and chemicals are necessary for expanding biomass utilization (Kankanamge, 2013). Main current biomass technologies are (Saglam, 2010);

- Gasification of biomass to gaseous products
- Pyrolysis of biomass and solid wastes to liquid, solid and gaseous products
- Conversion of biomass to a pyrolytic oil (biofuel) for vehicle fuel
- Supercritical fluid extractions of biomass to liquid products
- Liquefaction of biomass to liquid products
- Hydrolysis of biomass to sugars and ethanol
- Aneorobic digestion of biomass to gaseous products
- Biomass power for generating electricity by direct combustion or gasification and co-firing of biomass with coal
- Biological conversion of biomass and waste (biogas production, wastewater treatment)
- Biomass densification (briquetting, pelleting)
- Biomass energy conservation in households and industry
- Conversion of biomass to methanol and ethanol for internal combustion engines

Biomass derived energy can be obtained from major methods; thermo-chemical or bio-chemical processes. Thermo-chemical processes have received increasing attention since they are generally much faster and require a much less reaction time in comparison to bio-chemical or biological processes (Bridgwater, 2001). Moreover, a wider range of feedstock can be easily converted into energy with thermo-chemical processes compared to inefficiency with bio-conversion processes for some biomass feedstock (Hemmes et al., 2003). Biochemical technologies involve biomass transformations operated by micro-organisms and bacteria. Anaerobic fermentation is the most popular technology in the biochemical technologies. In this process, specific bacterias are able to assimilate some biomass substrates in order to grow in the absence of oxygen. Carbon dioxide and methane are produced by the metabolic activity of such

microorganisms. The resulting gas can be burned in internal combustion engines or turbines to provide both thermal and electrical energy. The other large area of biomass-to-energy conversion technologies is represented by thermochemical processes.

2.4.1 Thermochemical Conversions

Combustion, pyrolysis, gasification, and liquefaction are the common thermochemical conversion processes. Thermochemical processes are conducted under high temperature processes. Depending on the selected thermo-chemical process, the products could be in form of solid materials (e.g., charcoal), liquid fuels (e.g., bio-oils), and gases (e.g., fuel gases, syngas).

Pyrolysis of biomass is the heating of solid biomass in an inert atmosphere at temperatures between 300 - 600°C, where charcoal, bio-oil, or fuel gas are the products. Other terms used for pyrolysis include carbonization, wood distillation, destructive distillation and dry distillation (Sjöström, 1981). By changing the rate of heating and the final temperature, it is possible to modify the proportions of the products, e.g. the target product through flash/fast pyrolysis of is the bio-oil. Slow pyrolysis (slow heating rate) is used for the biomass conversion to charcoal. This method requires relatively slow reactions at low temperatures to maximize solid char yield). Fast pyrolysis or flash pyrolysis (Bridgwater, 2001) is a process in which dry biomass is heated rapidly to produce vapors that can be condensed to a liquid product that is usually indicated as bio-oil. This method requires very high heating and heat transfer rates (Vigouroux, 2001).

Biomass liquefaction produces liquids as primary products, usually at moderate temperatures 250 to 600°C. Liquefaction can be divided into two methods; thermochemical and hydrolytic liquefaction. Thermochemical liquefaction is a pyrolytic processing coupled with addition of H_2 , CO and CO_2 in the presence of catalysts. The hydrothermal liquefaction involves direct liquefaction of biomass, with the presence of water and perhaps some catalysts, to directly convert biomass into liquid oil. This process requires a temperature with a

reacting temperature of lower than 400°C (280-370°C) and 100-250 bars of pressure where the water is still in the liquid form.

For the abundant lignocellulosic biomass like wood or straw, fast pyrolysis has been selected as the most economic and convenient pre-treatment method for liquefaction. Fast thermal decomposition of dry lignocelluloses at about 500°C in the absence of oxygen generates a high yield of pyrolysis liquid and low yields of pyrolysis char and gas. The small amount of pulverized pyrolysis char can be completely suspended in about twice as much pyrolysis liquids to form a stable bioslurry or biosyncrude. This suspension is warmed up for viscosity reduction and transferred with a screw or plunger pump into the highly pressurized gasifier chamber for pneumatic atomization with pressurized oxygen. The biosyncrude is well suited for energy-dense storage and transport, resulting in lower transportation costs and large biomass delivery areas.

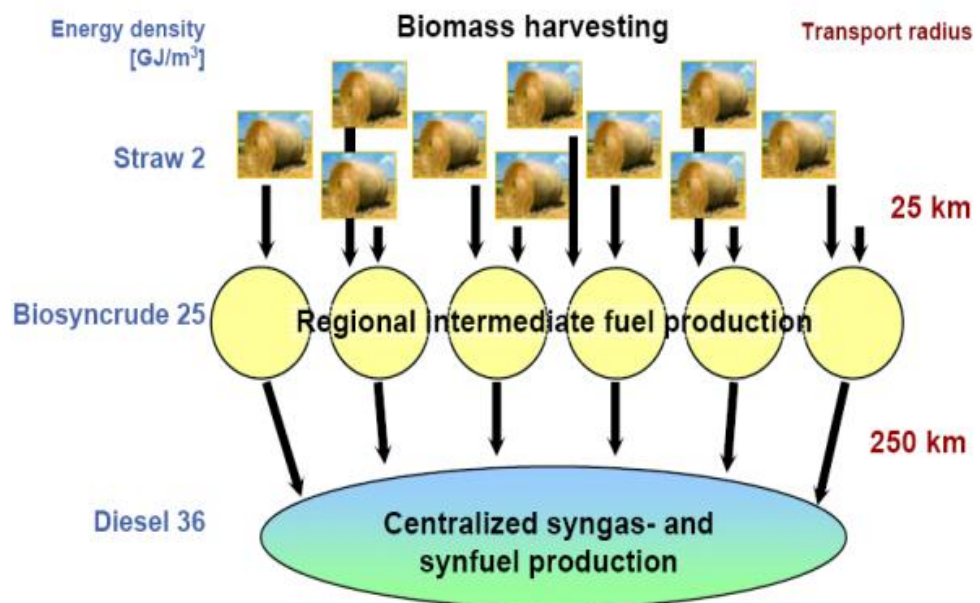


Figure 2.4.1.1 Flow scheme of the Karlsruhe bioliquid process.

The volume reduction and thus energy densification is considerably higher for straw than for wood. It is expected that for this kind of process, low-grade biomass of low volumetric energy density is much more similar to straw than to wood. An innovative approach for the bioliquid concept was developed at Karlsruhe Institute of Technology (KIT) in Germany (Figure 2.4.1.1). Figure 2.4.1.2 shows a photo of bioliquid Process in KIT, Germany. Schematic supply areas for fast pyrolysis plants in Germany were given in the Figure 2.4.1.4. Biosyncrudes produced in many regional fast pyrolysis plants with ca. 0.1 GWth biomass input (ca. 200 t/a airdry lignocellulose) can then be transported economically and in an environmentally friendly fashion in silo wagons on electrified rail over very long distances to a large, central biosynfuel and chemicals production complex (biorefinery) with an input capacity of several GWt. The flow diagram of the bioliquid process was given in the Figure 2.4.1.3. For example, as seen from the Figure 2.4.1.1, straw input (2 GJ/m^3) was transported to 25 km distance for regional intermediate fuel production. From this region, biosyncrude (25 GJ/m^3) is transported to 250 km distance for the centralized syngas-and synfuel production. From this point, straw energy was increased to 36 GJ/m^3 as diesel.



Figure 2.4.1.2 A photo of bioliquid Process in KIT, Germany.

Different biomass and carbon feedstock

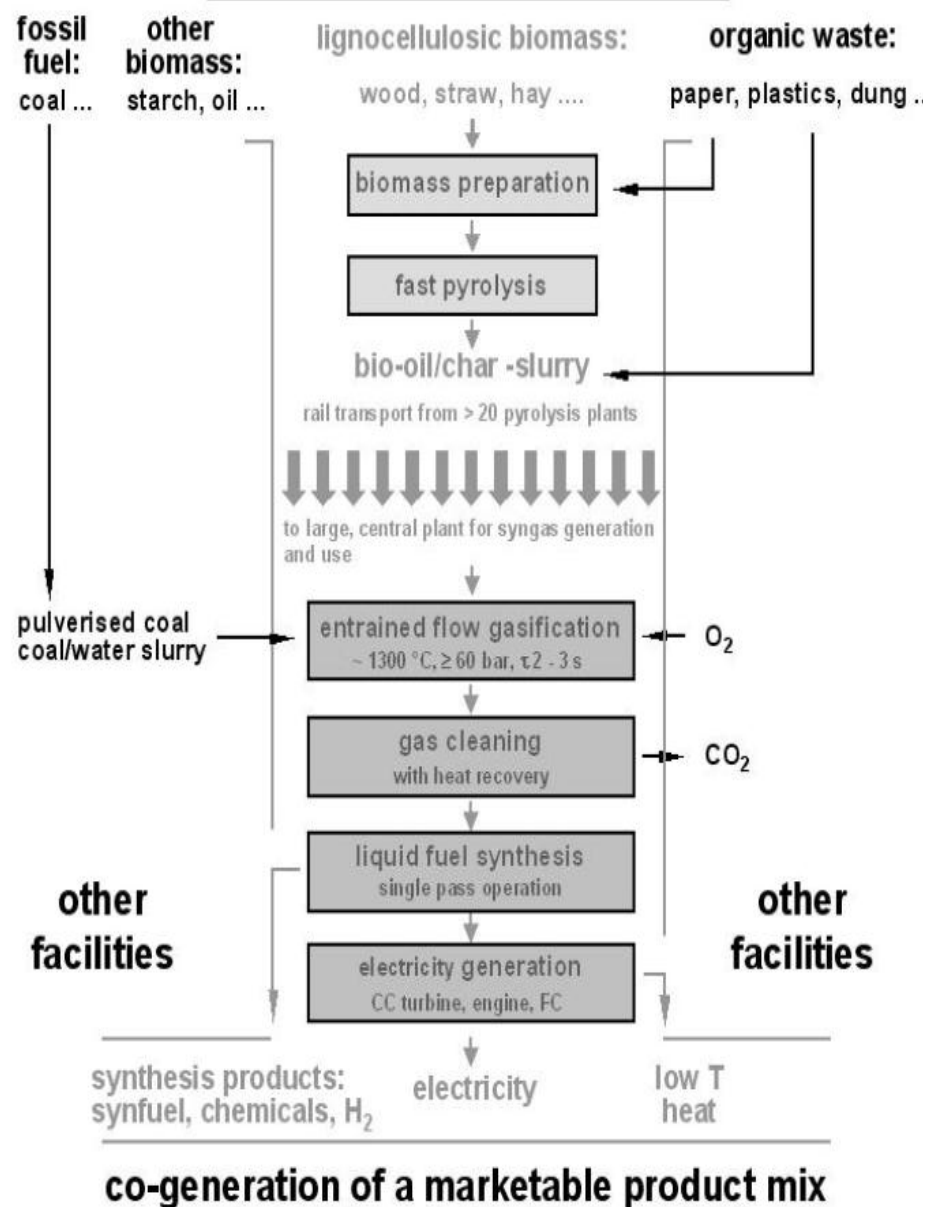


Figure 2.4.1.3 Flow diagram of the bioliquid process (Dahmen et al., 2012).

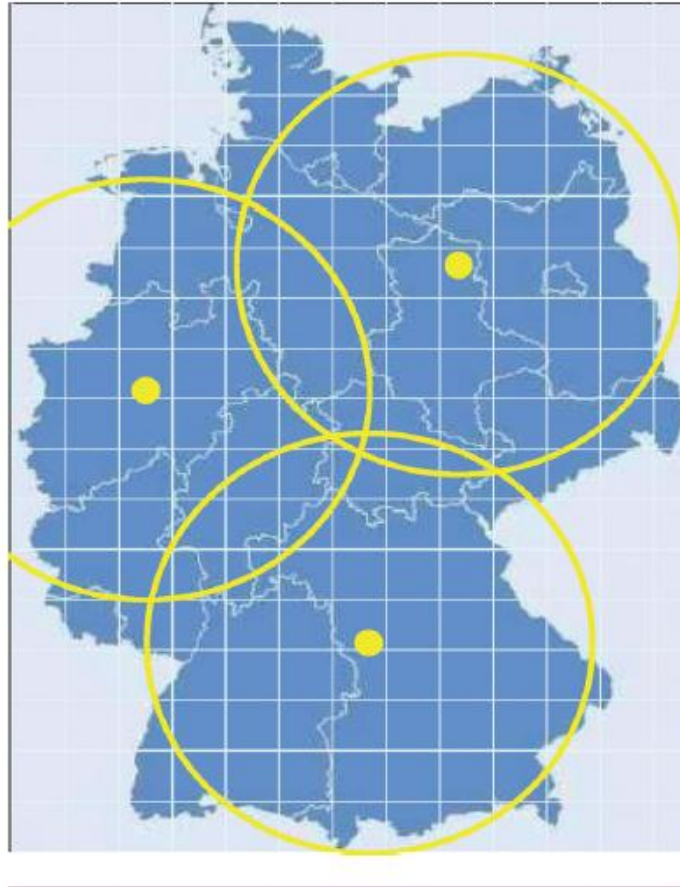


Figure 2.4.1.4 Schematic supply areas for fast pyrolysis plants in Germany (Henrich et al. 2009).

Gasification is an effective thermochemical route to convert carbon containing feeds into carbon monoxide, hydrogen, carbon dioxide and methane by applying heat under pressure in the presence of steam and controlled amount of oxygen. Temperature for gasification is generally higher ($>800^{\circ}\text{C}$) than pyrolysis operating temperature. Produced fuel gas by the gasification can be combusted, generating heat, or used in an engine or turbine for electricity generation. The produced gas can be also further processed towards to produce more hydrogen by water-gas shift reaction and methanol or liquid hydrocarbons by Fisher-Tropsch synthesis. The most important reactions during gasification are given in the Table 2.4.1.1 (Vigouroux, 2001).

Table 2.4.1.1 The most important gasification reactions.

Reaction	ΔH_{298} (kJ/mol)
$C + \frac{1}{2} O_2 = CO$	-111
$C + O_2 = CO_2$	-390
$CO + \frac{1}{2} O_2 = CO_2$	-254
$H_2 + \frac{1}{2} O_2 = H_2O$	-242
$C + 2H_2O = CO_2 + 2H_2$	+88
$C + H_2O = CO + H_2$	+131
$C + CO_2 = 2CO$	+172
$C + 2H_2 = CH_4$	-71
$CO + 3H_2 = CH_4 + H_2O$	-206
$CO + H_2O = CO_2 + H_2$	-41
$CO_2 + 4H_2 = CH_4 + 2H_2O$	-165

Each thermochemical process has advantages and disadvantages, and deciding on which process to apply is based generally on the optimization of factors including feedstock cost and availability, capital cost, upgrading requirements, marketing, etc.

2.5 Supercritical Water Gasification

The interest of supercritical water, as a reactive medium is due to its specific transport and solubilization properties. Indeed, in such conditions, water undergoes significant variations of its physical properties, like a decreasing of the dielectric constant, thermal conductivity, ion product and viscosity while the density only decreases slowly. Figure 2.5.1 shows some water properties with temperature and pressure. In this technology, the solvent properties of water can be adjusted by changing the temperature and the pressure. For example organic species and gases could be miscible with water above its critical point because the dielectric constant of water decreases. Supercritical water acts as a homogeneous non-polar solvent of high diffusivity and high transport properties, able to dissolve any organic compounds and gases. In such a process, hydrogen can be produced at thermodynamic equilibrium because of the operating conditions. Chemical reactions with high efficiencies can be obtained in the case of a water–organic mixture without interfacial transport limitations. Physical properties of water that change with temperature and pressure were given in the Table 2.5.1.

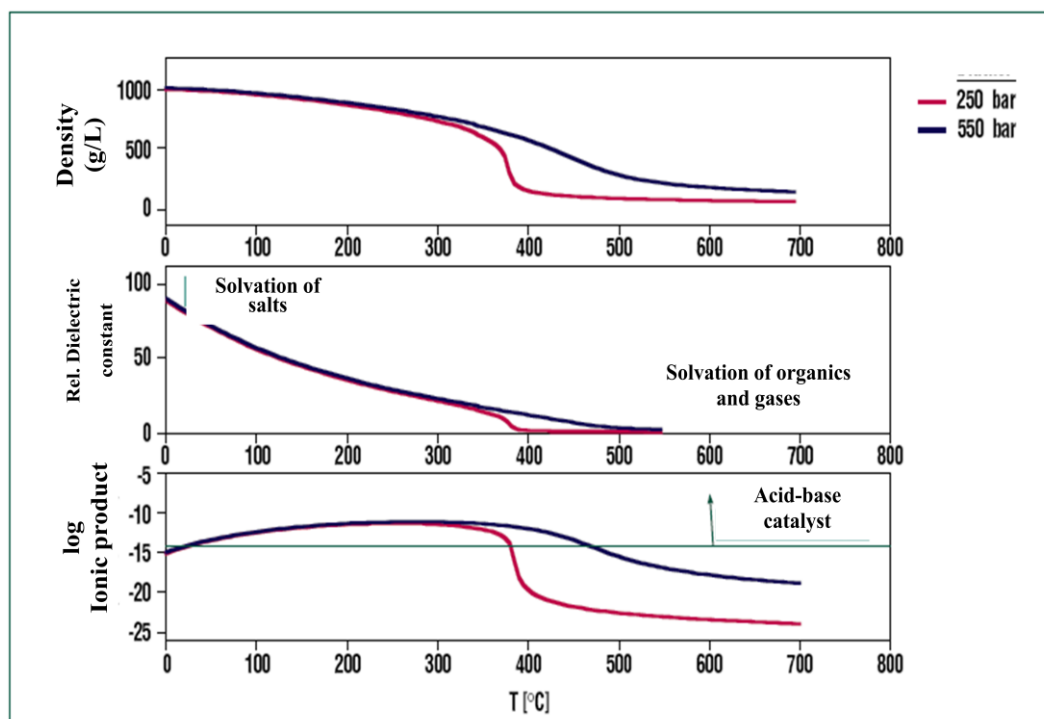


Figure 2.5.1 Change of some water properties with temperature and pressure.

Table 2.5.1 Physical properties change of water with temperature and pressure.

	Normal Water	Subcritical water	Supercritical water	Supercritical water
Temperature, T (°C)	25.0	250.0	400.0	400.0
Pressure, P(MPa)	0.1	5.0	25.0	50.0
Density, P (g/cm³)	0.997	0.8	0.17	0.58
Dielectric constant, e (-)	78.5	27.1	5.9	10.5
Ionic product, pKw (-)	14.0	11.2	19.4	11.9
Heat capacity, Cp (kJ/kg.K)	4.18	4.8	13.0	6.8

For the conversion of biomass to energy or energy carriers, the moisture content of the biomass is of crucial importance in view of the net lower heating value. The net lower heating value is defined by Potic (2006);

$$\text{LHV}_{\text{net}} = (1 - X_{\text{moisture}}) \times \text{LHV} - X_{\text{moisture}} \times \Delta H_{\text{vap}}$$

in which X_{moisture} is the mass fraction of moisture in the biomass, LHV is the lower heating value of the dry fraction and ΔH_{vap} the enthalpy of vaporization of water. This definition of the net lower heating value thus includes the energy required for vaporization of the moisture. One important drawback of the supercritical water gasification is the need for preprocessing of the feed to reduce its water content. Supercritical water (SCW) can be used as both reaction media and reactant simultaneously. Water as reaction media is safe, non-toxic, inexpensive and readily available. Supercritical water (SCW) as a reaction media greatly decreased the temperature requirement of gasification. However, these processes require higher pressures and thus need more consideration regarding reactor construction (Matsumura et al., 2005).

The conversion efficiency of thermal gasification is generally higher than other options, but above a fuel moisture content of 31%, the conversion efficiency of thermal gasification falls below that of supercritical water gasification as seen in the Table 2.4.2 (Yoshida et al., 2003). So that supercritical water gasification offers a good option for gasification of high moisture biomass.

Table 2.5.2 A comparison of energy conversion efficiency of different options for biomass conversion (Data collected from Yoshida et al., 2003).

Moisture content in feed	5%	31%	55%	75%
Biomass Conversion Process	Energy conversion efficiency			
Thermal Gasification	61	55	47	27
Pyrolysis	57	53	45	27
Liquefaction	39	37	36	34
Anaerobic Digestion	31	31	31	31
Supercritical Water Gasification	55	55	55	55

2.5.1 Thermophysical Properties of Water at Hydrothermal Conditions

The phase diagram of water (Figure 2.5.1.1) shows the phases are present at any given temperature and pressure. Water above its critical temperature (374.1°C) and critical pressure (221 bar) is known as “supercritical water”. Water below the critical temperature, 374.1°C but at a pressure above its saturation pressure is referred to as “Subcritical water”.

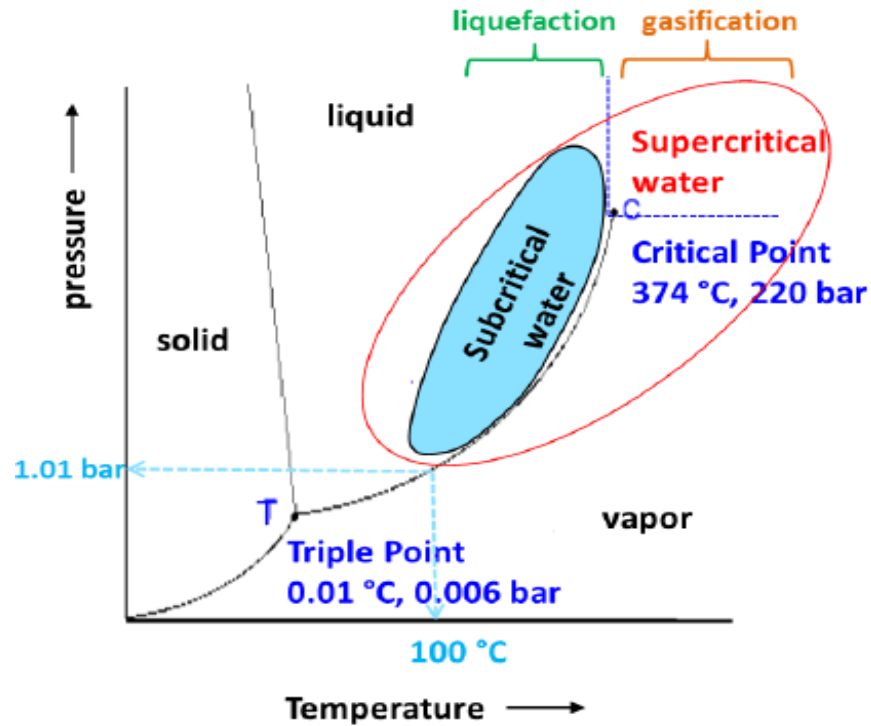


Figure 2.5.1.1 Phase diagram of water.

Above the critical pressure, water has a “pseudo-critical” temperature, where water experiences a transition from liquid-like to gas-like behavior. The pseudo critical temperatures for a given supercritical pressure can be estimated within above and on the critical pressure by the relation given below. This relation is valid up to 80MPa (Malhotra, 2006). Above the critical pressure, the density change in water is gentle and modest across its “pseudo-critical” temperature, where a transition from liquid-like to vapor-like state takes place (Basu, 2009).

Density, viscosity and dielectric constant are three main properties that influence the gasification of biomass. Supercritical water is well suited for gasification on account of its favorable values for all these three properties, and these are discussed briefly below.

2.5.1.1 Density

The density of water is a function of temperature and pressure (Figure 2.5.1.1.1). As can be seen from the Figure 2.5.1.1.1 below the critical pressure (221 bar) a phase change occurs. This is marked by the straight vertical lines, indicating sudden drop of density, as water passes from the liquid to vapor state. Increasing pressure increases the density. In the supercritical region, the water density can be changed from liquid-to gas like by varying the temperature and pressure without any phase transition. So that water can behave almost as non-aqueous fluid at supercritical conditions. The dissolving power of a fluid is exponentially dependent on its density (Chrastil, 1982). While the dissolving power of a supercritical water is generally lower than the liquid water, it is the combination with high miscibility that makes it such an excellent reaction medium.

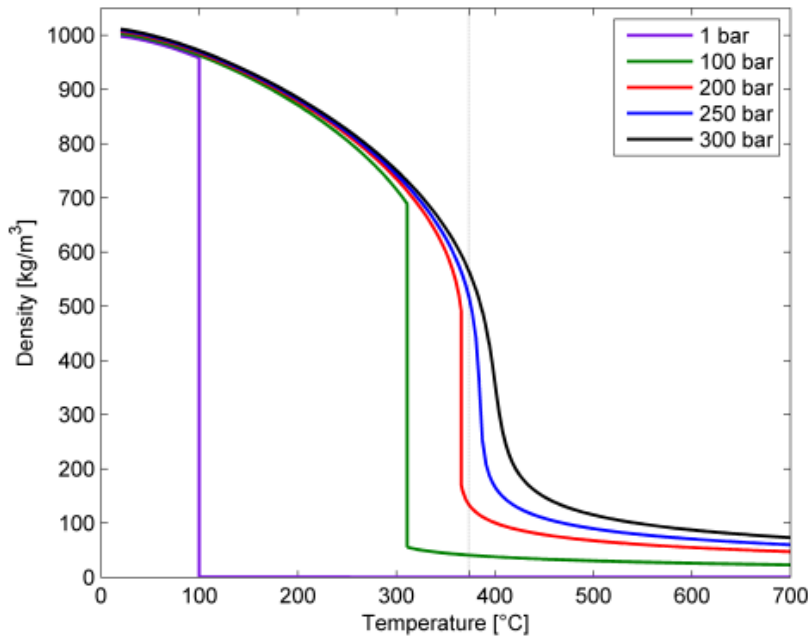


Figure 2.5.1.1.1 Density of water as a function of temperature and pressure (Castello, 2013).

2.5.1.2 Dielectric Constant

The polarity of a solvent is a remarkable behavior of the static dielectric constant ϵ . The polarity of a solvent expresses the ability of its molecules to form dipoles. This property determines whether a certain substance can be dissolved in a certain solvent or not. A polar solvent can dissolve polar solutes, while non-polar solutes get dissolved in non-polar solvents.

Water at room temperature has a dielectric constant of around 80, which makes it a quite strong polar solvent (Castello, 2013). Figure 2.5.1.2.1 shows dielectric constant (ϵ) of water as a function of temperature and pressure. When it is heated and compressed up to the supercritical state, the dielectric constant drops to values typical of non-polar solvent. In Figure 2.5.1.2.1, the trend of the dielectric constant is reported, calculated according to (Uematsu et al., 1980).

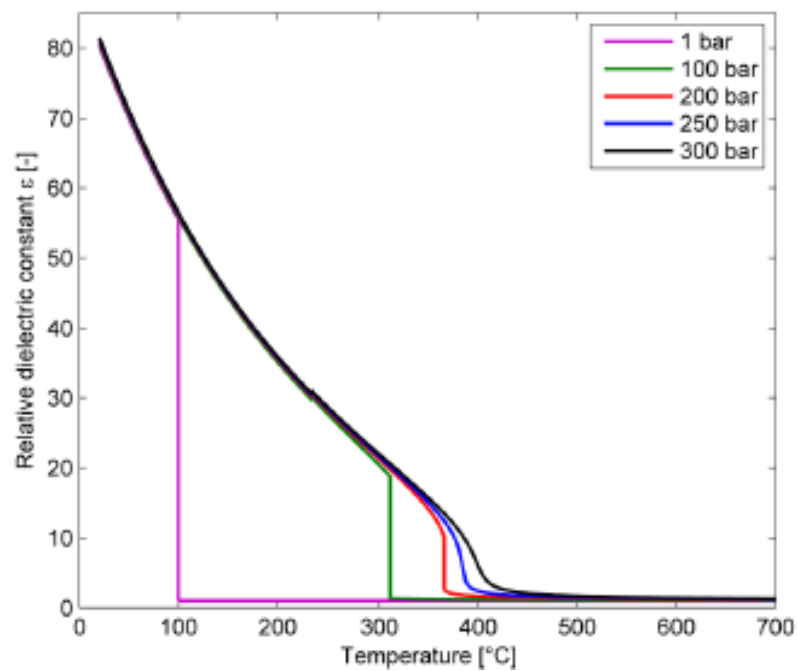


Figure 2.5.1.2.1 Dielectric constant (ϵ) of water as a function of temperature and pressure (Castello, 2013).

2.5.1.3 Ion Product

The ion product is defined as the product between the molar concentration of ions H_3O^+ and OH^- which are in equilibrium with non-dissociated water molecules (Castello, 2013). The reaction at hydrothermal conditions involving polar or weakly polar solutes are influenced by this property. At room conditions, the ionic product of pure water K_w is $10^{-14} \text{ mol}^2/\text{kg}^2$ or, in other words, its $\text{p}K_w$ is 14. This gives a measure of how many ions are present, which is determining for acid-base equilibria and for the selectivity towards certain types of reaction (for example, ionic pathways). As the temperature of water increases at constant pressures, the value of K_w first increases and decreases after the critical point. The high ion product supplies a high concentration of H^+ and OH^- near the critical point. Therefore, water may behave as acid or base. Figure 2.5.1.3.1 shows the trend of $\text{p}K_w$ for water at sub- and supercritical conditions, estimated by means of the interpolation formula of (Marshall et al., 1981).

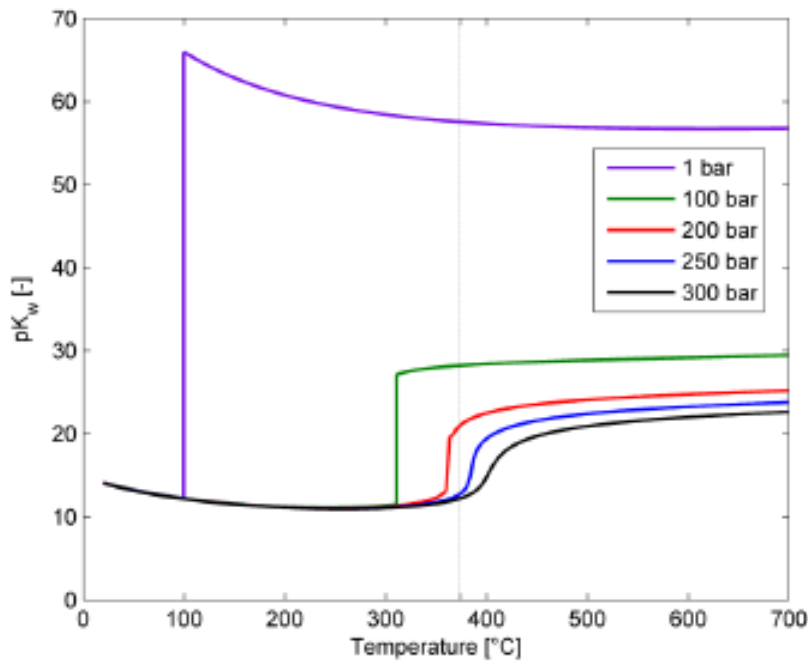


Figure 2.5.1.3.1 Value of $\text{p}K_w$ ($-\log K_w$) of water as a function of temperature and pressure (Castello, 2013).

All of these special properties of the water results in a number of advantages of gasification in supercritical water as compared to dry gasification process;

- No drying of the wet biomass is necessary,
- A hydrogen rich gas with low CO content can be produced in one step,
- CO₂ is the second main product, can easily be separated at high pressure due to its high solubility in water,
- Less tar and coke are formed,
- Hydrogen is available at high pressure, so that it is not necessary to compress for transportation,
- Short reaction times, since high space time yield results from the use of a high pressure process with the high reactivity of the biomass under these conditions.

Main problem of supercritical water gasification is the tar and ash formation. Another problem is that Ni and many of the other metallic catalysts can suffer severe corrosion in supercritical water. At the same time, heating of the biomass slurry in the inlet tube of a reactor is likely to cause fouling/plugging problems because the thermal decomposition (>250°C) starts already far below the desired reaction temperature. Many research group laboratories (e.g., Hawaii University, Hiroshima University, Forschungszentrum Karlsruhe (FZK)-Germany, Twente University, Osaka Gas, Pacific Northwest National Laboratory, and etc.) are aimed to prevent the problems by studying the effects of the various parameters on biomass gasification in supercritical water. Although many small reactors have been used in, large scale industrial plants do not exist yet. Forschungszentrum Karlsruhe (FZK) in Germany is the largest plant working on supercritical water gasification. This large scale reactor with about 100 L/hour capacity was built to investigate the commercial gasification of wet residues. This pilot plant called, VERENA (Figure 2.5.1.3.2) is the first completed continuous operating plant worldwide for SCWG. Employing VERENA, SCWG of corn silage produces a gas product consisting of 36 vol% methane and 45 vol% hydrogen. The first generation of pilot plant for supercritical water gasification with a capacity of 30 L/hour was developed at the University of Twente, Netherlands (Nanou, 2013).

The most studies, appearing in the literature, are done with the cellulose which is the main constituent of plants and the glucose. The other group works were done with the lignin, the phenol representing lignin, and 1,2 dihydroxybenzene. However, any study carried out with the extractives and hemicelluloses or monosaccharide forming hemicelluloses were not appeared in the literature. Only there are studies with xylan and xylose. In this respective, xylose, arabinose and pectin as model compound for the hemicellulose, tannic acid, gallic acid, 1,2,3 trihidroksibenzene and 1,3,5 trihidroksibenzene for extractives were selected for this study. Supercritical water gasification of these model compounds were performed in a batch reactor system at high temperatures (400, 500 and 600°C) and high pressures (20, 27.5, 35.0 and 42.5 MPa). The objective of this study was to elucidate the simultaneous effect of the high reaction temperature, high pressure and catalyst on the gas and liquid product distribution. The influences of temperature, pressure and catalyst were examined in relation to the maximum yields of the H₂ and CH₄ gases and the liquid products. The deficiency in the literature will be eliminated by clarifying the reaction mechanism and the attitudes in the supercritical water of the hemicelluloses and extractives.



Figure 2.5.1.3.2 A photo of feed system of VERANA, KIT, Germany.

3.0 LITERATURE REVIEW

As a result of the increase in globally energy demand, the dependence on fossil fuels has increased rapidly. With declining fossil fuel resources, combined with political concerns, it is imperative to develop economical and energy-efficient processes. On the other hand, since the beginning of industrialization, the greenhouse and toxic gas content, such as CO₂, SO₂, NO_x and other pollutant amounts in the atmosphere have been rising. Due to these facts, continuous effort has been made in exploration of renewable and clean alternatives.

Especially, renewable energy sources like solar energy, nuclear energy, hydrogen energy and biomass attract interest of many researchers. These can provide the source of renewable liquid, gaseous and solid fuels. Due to the many advantages and using areas of hydrogen, many research groups have tried to produce hydrogen. Approximately 95% of the hydrogen production comes from primarily fossil resources. Renewable-based processes like solar- or wind-driven electrolysis and photobiological water splitting hold great promise for clean hydrogen production; however, advances must still be made before these technologies can be economically competitive.

Biomass is considered the renewable energy source with the highest potential to contribute to the energy needs of modern society for both developed and developing world-wide economies. Since biomass is formed by fixing carbon dioxide in the atmosphere during the process of plant photosynthesis, biomass can lead to zero CO₂ emission in lifecycle. Currently, biomass contributes about 12 % of today's world energy supply, while in many developing countries it contributes 40–50 % energy supply. Biomass research is recently receiving increasing attention because of the probable waste-to-energy application. For example, about 2900 EJ energy can be obtained from 170 GT of vegetable biomass generated globally every year (Klingler, 2006, Ni 2006, Onken 1996). The biomass energy resource has many advantages such as lower price, less sulphur composition, less ash content and the feature of renewability. On the other hand, it also has some unfavorable aspects such as higher water content, lower unit thermal output, large volume, decentralized resource and unsuitable for collection, storage and transportation. But these disadvantages can be overcome. As long as suitable

measures are adopted, taking into account local conditions, using available science and technology, selecting a reasonable technical program, adopting advanced techniques, developing new energy conversion methods and paying attention to the energy utilization efficiency and economy of biological system, then biomass resources can be used efficiently.

Many types of biomass resources can be used for energy production. Generally they can be divided into two categories:

- (i) Growing plants specially for energy use (energy crops); woody energy crops, industrial crops, agricultural crops and aquatic crops
- (ii) The residues and wastes from plants that are used for other things; agricultural residues and waste, forestry waste and residues, industrial and municipal wastes.

Wet biomass cannot be converted economically by traditional techniques, because of the large amount of energy required for the evaporation of water (Matsumura, 2002). Supercritical water gasification may become an important technology for converting wet biomass to a pressurized and clean medium caloric value gas with high hydrogen content. Supercritical water gasification is a novel method being studied and developed more than thirty years. The most important potential sources for wet biomass materials with a more than %80 water contents are unevaluated parts of all plants, vegetables and fruits residues which are being products of photosynthesis and these can be used for sustainable production of hydrogen. The change of the water properties with increasing temperature leads to a change of the reaction pathways from ionic to free radical. Kruse et al. (2003) has explained the chemistry of biomass degradation by a simplified reaction scheme of liquifaction and/or gasification with regards to the identified key compounds and the findings from experiments with model compounds according to the reaction temperature sub or supercritical conditions.

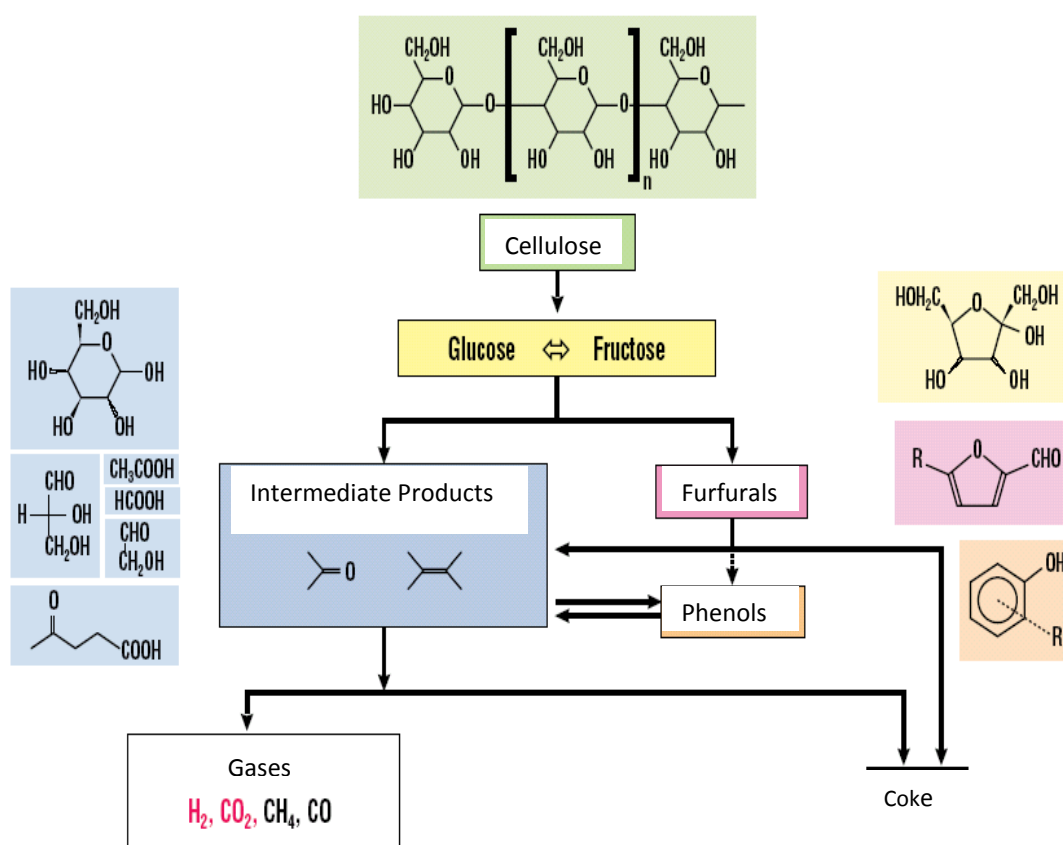


Figure 3.1 Simplified reaction scheme of liquifaction and/or gasification with regards to the identified key compounds and the findings from experiments with model compounds (Kruse et al., 2003).

When compared with the conventional gasification proceed at normal pressure, the most important advantages of the supercritical water gasification are considered as follows: This method is appropriate for production of both H_2 and CH_4 , pre-drying of biomass materials are not necessary, it is operated at lower temperatures, smaller reactor volumes are required because of high reaction rate, CO formation is very low, thus reforming process is not required, and formation of tar and coke is much lower. Corrosion and the way of biomass feeding to reactors are the most important problems which have to be overcome.

A number of researchers have investigated the hydrothermal gasification method for biomass conversion. For proper development of hydrothermal gasification process, data concerning the influence of the process conditions (temperature (T), pressure (P), reaction time (t), concentration (c)) and also

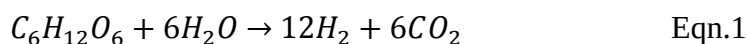
biomass type, particle size, catalyst type, catalyst amount on the gas yields and by product formation (char, liquid intermediates) are needed. The first study on supercritical gasification of wood is done by Modell in 1977 and a patent was issued in 1978 (Modell 1977 and 1978). Modell reported the effect of temperature and concentration on the gasification of glucose and maple sawdust in water in the vicinity of its critical state. In 1985, Modell has given a review of gasification and liquefaction of forest products in supercritical water (Modell, 1985).

Lignocellulosic biomass is mainly composed of cellulose, hemicellulose, lignin, and extractives and the compositions vary depending on the source of the biomass. These major structural components generally have rough compositions of 30-50% of cellulose, 20-40% of hemicelluloses, 15-25% of lignin and 1-3% extractives. The composition of these constituents can vary from one plant species to another. For example, the extractive ratio can be increased to 40-50% for some biomass species. Cellulose is a homopolysaccharide consisting of a linear chain repeating units of cellobiose - a dimer of β -D-glucose. Hemicellulose is chained and amorphous biopolymer composed of the primary monomer constituents hexoses and pentoses. Lignin is a complex high molecular weight compound with three most prevalent monomers as p-coumaric alcohol, coniferyl alcohol and sinapyl alcohol. Waxes, terpenes, aliphatic and aromatic hydrocarbons, volatile oils, fatty acids, aliphatic and aromatic acids and their salts, alcohols, phenols and phenolic constituents such as, tannins and flavonoids, aldehydes, ketones and quinines, esters and ethers comprise the extractives.

Cellulose, lignin, hemicellulose and extractive substances show different attitude in supercritical water gasification. Therefore, so important disparities are observed in the gasification efficiency and the product distribution. Many studies have been done for the purpose of the industrial feasibility of the method. The important parts of them are the scientific researches, that are fevered to understand the attitude of the main components in the plant structure in SCWG and to clarify the reaction progress. The most studies, appearing in the literature, are done with the cellulose which are the main constituent of plants and the glucose, monosaccharide as the model compound and the reaction mechanism were studied to clarify. The other group works were done with the lignin, the main important constituent of plants, the phenol representing lignin, and 1,2 dihydroxybenzene

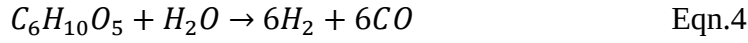
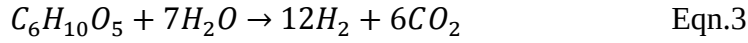
Antal's first report on supercritical conversion of biomass-related organics was in 1990. In this study glucose was converted largely to H_2 and CO_2 at $550^\circ C$ (Antal, 1990). Mok and Antal performed a study of the uncatalyzed solvolysis of whole biomass and hemicellulose in hot compressed liquid water (Mok and Antal, 1992). These first studies show that complete gasification of glucose can occur at $600^\circ C$, 34.5 MPa and in 30 second residence time. Antal research team developed a method in 1996 to extend the catalyst life and measured the rate of carbon catalyst gasification in supercritical water (Antal, 1996). Cellulose and lignocellulose materials gasification in high pressure steam were carried out by Minowa, Yokoyama and Ogi studies. At a temperature of $200-374^\circ C$ and pressure of 17 MPa by using reduced metal catalyst, hydrogen formation was investigated (Minowa et al. 1995a; Minowa et al., 1997; Minowa and Fang, 1998; Minowa and Ogi, 1998; Minowa and Inoue, 1999). Minowa et al. performed methane production from cellulose in 1994 and 1995 (Minowa 1994, 1995b). In 1997, Matsumura et al. has published a review on glucose conversion in supercritical water of the University of Hawaii work (Matsumura, 1997a). Also in 1997, Matsumara et al. studied the gasification of an activated carbon in supercritical water (Matsumara, 1997b). Antal and Xu presented data on the starch-biomass paste approach to water gasification under supercritical conditions in 1998 (Xu and Antal, 1998). Antal et al. reported further results with pastes of potato wastes, wood sawdust and various starch gels in 1999 (Antal, 1999).

In a similar study, the idealized reaction for glucose to H_2 and CH_4 was represented in the following equation by Kruse et al. At high temperatures ($600-700^\circ C$), hydrogen is the main product of the biomass conversion in supercritical water (Eqn.1), at low temperatures ($200-400^\circ C$), methane is produced from biomass (Eqn. 2) (Kruse et al., 2007);



The choice of relative high temperature is an outcome of equilibrium considerations predicting methane as main burnable product at relative low and hydrogen as main product at higher temperatures (Tang et al., 2005). Montilva et

al., represented the idealized reaction for cellulose as the following reactions by the Equations 3 and 4 (Montilva, 2007):



For cellulose as model compound for biomass idealized conversion to CH_4 would follow the Equation 5:



As the temperature increases, amount of H_2 and CO_2 in gases product increases, but CO decreases. This decrease can be explained by the promotion of water gas shift reaction (**WGSR**):



The operation parameters, such as reaction temperature, reaction pressure, residence time, heating rate, feed concentration, biomass type, biomass particle size, reactor design and catalyst play an important role in product efficiency and formation of tar. Reaction temperature is the most important parameter that influences the performance of a hydrothermal gasification. Although, operation at lower temperatures is economically favored comparing to higher temperatures in terms of the operating costs, temperature has a significant effect on the specific yield of gasification especially in absence of catalyst (Guo et al, 2007). There are many studies on hydrothermal conversion of wet biomass either at high or low temperatures. Kersten et al. studied supercritical water gasification of 1 wt.% glucose in a capillary reactor. Experimental results shows that increasing reaction temperature raises gas production for both methane and hydrogen. This effect is more intense for hydrogen, but methane gas is still slightly increased. For instance, from 500 to 800°C, the hydrogen yield increases from almost 1 to 5.5 mol/mole of glucose, while this number goes from 0 to 0.75 mol/mol for methane using glucose (Kersten et al., 2006).

The rate of formation for all gas species increased with temperature. It also increased the mole fractions of H_2 and CH_4 in the gaseous products. Manipulating cellulose loading and water density provided an efficient means to control the product selectivity, since the relative amounts of H_2 and CH_4 were strongly influenced by these two process variables. In general, higher H_2 yields were obtained at the longer reaction times, higher water densities, higher cellulose loadings, and higher temperatures.

Kruse et al. (2005) studied the conversion of biomass in sub- and supercritical water. Their biomass was baby food which has the formula $CH_{1.87}O_{0.98}N_{0.02}S_{0.001}$ (through elemental analysis). In this study, they identified phenols, furfurals, acids and aldehydes as key components in their liquid by-product. They monitored gas production and found that increasing the temperature increased the amount of carbon (mainly CO_2 in the gas phase). Alkanes and alkenes up to cis/trans butane were identified through GC. They contend that at temperatures lower than $374^\circ C$, intermediate compounds are formed and are preferred over gas formation itself at ionic water conditions. However, at supercritical conditions where the lower density of water encourages free-radical reactions, gases are formed preferably.

Lu et al. (2006) aimed to prevent the plugging problem by studying the effects of the various parameters on biomass gasification in supercritical water. These parameters include pressure, temperature, residence time, reactor geometrical configuration, reactor types, heating rate, reactor wall properties, biomass types, biomass particle size, catalysts and solution concentration. Biomass model compounds (glucose, cellulose) and real biomass were used in this work. All the biomasses have been successfully gasified and the product gas was composed of hydrogen, carbon dioxide, methane, carbon monoxide and a small amount of ethane and ethylene. Generally, 40% molar fraction of H_2 was reached. Hydrogen production by biomass gasification was influenced by many operating parameters. The dominate reaction pathway changed by pressure when temperature was above the critical point. The gas yield was very sensitive to the reactor temperature. From an economic point of view, operating temperature above 973K and a pressure about 25MPa is preferable. Long reactor residence

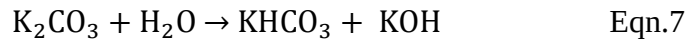
time and high heating rate are favorable to gas yield. In this paper, some suggestions for overcoming the reactor plugging were provided as the following: (1) high reaction temperature, (2) high heating rate in the entrance region of the reactor, (3) using catalyst and (4) innovative reactor designs (Lu et al., 2005).

The subcritical and supercritical water gasification of cellulose, starch, and glucose as representative biomass model compounds and biomass in the form of Cassava waste has been investigated by Williams et al. (2006) in a heated batch reactor. Cassava (*Manihot esculenta* Crantz) waste is the solid waste produced as a consequence of starch production. This pulp contains a high starch content (50–60% dry basis), causing an environmental problem with disposal. The influence of temperature was examined in relation to the yield of the product gases in the subcritical and supercritical regime of water. For the model compounds and the Cassava waste, the main gases produced were carbon dioxide, carbon monoxide, hydrogen, methane, and other hydrocarbons, and there was significant production of oil and char. The cellulose and starch are polysaccharide polymers based on the glucose monomer, $C_6H_{12}O_6$, but they have different chemical structures and physical properties. The results have shown that these differences produce significantly different product yields. For example, the char yield from cellulose supercritical water gasification was much higher than that from starch. In addition, the oil, carbon dioxide, and hydrogen yields were lower and carbon monoxide and C1-C4 hydrocarbons were higher for cellulose than for starch. The results for the sub- and supercritical water gasification of glucose showed that there was significant production of hydrogen gas. In terms of the conversion of the hydrogen contained in the sample to hydrogen gas, the conversion was greatest for glucose, followed by starch, followed by cellulose. Cassava biomass gasification produced a low conversion of the hydrogen contained in the chemical structure to hydrogen gas, but was similar to that found for cellulose. Consequently, in predicting the behavior of biomass feedstocks under supercritical water gasification conditions via the use of model biomass samples, the chemical structure of the compounds which also relate to their physical properties should be taken into consideration in addition to the chemical composition of the model biomass polymer (Williams et al., 2006).

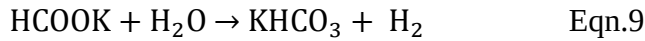
Different types of reactors such as batch, tubular flow, continuous and capillary reactors can be used for the hydrothermal gasification. The design of the batch reactor is simple and they are suitable reactors to examine the gas production yield and carbon conversion into hydrogen or methane. There are several different types of batch reactors. Disadvantage of the batch reactor is that it is difficult to isolate the different reactions occurring during the heat-up and the cool-down stages. Thus it is not possible to study reaction with very short residence time. Tubular flow reactor provides a continuous gasification with a short residence time, but plugging is a major problem. The continuous flow reactor is more complex, it is an integration of batch and tubular flow reactor. However, these reactors are challenging to operate as plugging may occur and additional energy is required for stirring (Lu et al., 2006, Kruse 2008). Quartz capillaries as batch micro-reactors are very efficient in terms of being able to run at high speeds and are relatively inexpensive tests. Additionally, various visual techniques can be used to record events occurring inside the capillary (Mozaffarian et al., 2004).

Biomass feedstocks, including corn- and potato-starch gels, wood sawdust suspended in a cornstarch gel, and potato wastes, were delivered by Antal et al. to three different tubular flow reactors by means of a “cement” pump (Antal et al., 2000). When rapidly heated to temperatures above 650 °C at pressures above the critical pressure of water (22 MPa), the organic content of these feedstocks vaporized. Extraordinary yields (>2 L/g) of gas with a high content of hydrogen (57 mol %) were realized at the highest temperatures employed in this work. There were effectively no tarry byproducts. The gas composition and gas yield are strongly affected by the reaction temperature. High entrance temperatures favored the methane steam-reforming reaction and resulted in the production of a hydrogen-rich gas with yields exceeding 2 L/g. Metals present in the Hastelloy reactor tube (i.e., Ni) appeared to catalyze the gasification and reforming reactions. Some biomass feedstocks (e.g., potato wastes) deactivated the reactor’s wall. Metals leached from the Hastelloy are found in the activated carbon catalyst bed within the reactor. Future work should be conducted in reactors with walls that do not suffer corrosion and do not catalyze the reactions of interest (Antal et al., 2000).

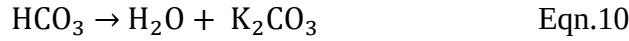
Principal type of catalysts for supercritical water gasification of biomass and biomass model compounds are alkali catalysts, metal catalysts and carbon based catalysts. Alkali catalysts such as K_2CO_3 , KOH , Na_2CO_3 , $NaOH$ are the primary homogeneous catalysts, easily miscible with the water and effective for supercritical water gasification. Alkali catalysts promoted sugar degradation while inhibiting the char formation, increase hydrogen and decrease CO yield by acceleration of the water gas shift reaction (Elliott et al., 2004, Matsumura 2005). The catalytic effects of K_2CO_3 can be explained by catalysis water-gas shift reaction via the formate formation ($HCOO^-K^+$) (Yanik et al., 2008):



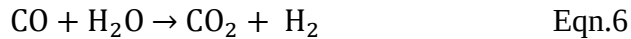
Hydrogen is obtained by reacting of formate with water:



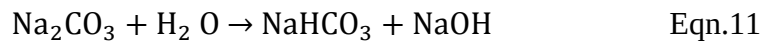
The catalytic cycle is completed by the decomposition of $KHCO_3$:



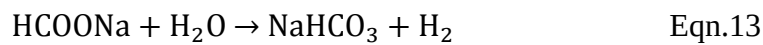
The overall reaction is (WGSR):



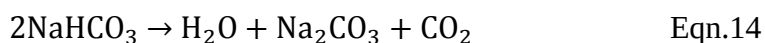
The catalytic effect of Na_2CO_3 is explained by the formation of formate salts as follows (Chen et al., 2006):



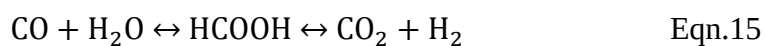
Formate salts reacts with water to produce hydrogen:



CO₂ is produced by the decomposition of NaHCO₃;



and by the reaction of CO with H₂O yield (WGSR), formic acid and later CO₂ and H₂



The effectiveness of heterogeneous catalysts, mainly containing metallic catalysts (Ni and Ru, etc.) have been used for hydrothermal gasification of biomass. Heterogeneous metal catalysts are attractive for gasification because their selectivity is better and recovering easier. However, the major challenge for using metallic catalysts for supercritical water gasification reactions is that the harsh condition of supercritical water gasification, which causes oxidation of the catalyst (Behnia, 2013). Azadi et al. represents an extensive literature review of heterogeneous catalysts in terms of activity, hydrogen selectivity and stability (Azadi et al., 2011). This review of Azadi could be served as a useful tool for the selection and design of new catalysts and for supercritical water gasification processes. Commercially available and laboratory prepared catalysts including supported metal catalysts, activated carbon, oxides, metal wires and other innovative catalysts are considered. A wide variety of supported nickel catalysts have been used for catalyzing supercritical water gasification (SiO₂, Al₂O₃, SiO₂-Al₂O₃, MgO, ZrO₂, etc.). Phenol, ethanol, cresol and glucose were used as model compound and lignin, cellulose, wood and etc. were used as biomass. Also ruthenium catalysts have been used for catalyzing supercritical water gasification by using similar support, models and biomasses. Ru as well as other noble metal catalysts usually have a higher metal dispersion compared to nickel catalysts, partly because of their milder reduction temperatures (Azadi et al., 2011).

Catalytic hydrothermal gasification of glucose, cellulose, fructose, xylan, pulp, lignin and bark have been studied in the presence of Ni/ α -Al₂O₃, Ni/hydrotalcite, Raney nickel, Ru/C, and Ru/ α -Al₂O₃ catalysts at 350°C in a batch reactor (Azadi et al., 2012). In this study they found that with nickel and ruthenium based catalysts high methane production was achievable. Zhang et al.

(2011a) studied gasification of a 5 wt.% aqueous glucose solution at 600°C. It was found that reduced nickel catalyst favored the water-gas shift reaction, and ruthenium suppressed tar and char production (Zhang et al., 2011).

Dolomite, trona, red mud (Fe-oxide containing residue from Al-production and etc. are mineral catalysts used for hydrothermal gasification. Yanik et al., investigated the effect of the type of catalyst on hydrothermal gasification of three specifically chosen samples of natural biomass. Biomass feedstocks, including lignocellulosic materials (cotton stalk and corncob) and the tannery waste, were gasified in supercritical water by the addition of catalyst. The catalysts used were K_2CO_3 , Trona ($NaHCO_3 \cdot Na_2CO_3 \cdot 2H_2O$), red mud and Raney-Ni. The gasification activity of Trona was similar to that of K_2CO_3 . The results indicate that iron based catalysts can also be effective in gasification of biomass. In conclusion, the supercritical water gasification of biomass by addition of red mud and Trona was said to be promising method to produce H_2 from biomass efficiently similar to gasification with commercial alkali catalysts.

Generally carbon catalysts (Wood charcoal, coal activated carbon, etc.) increased the carbon gasification efficiency while reducing the CO content. Milne et al. (1998) has reported that tar could be thermally cracked at temperature above 1273 K. The use of some additives (dolomite, olivine and char) inside the gasifier also helps tar reduction (Corella et al., 1999). Catalysts not only reduce the tar content, but also improve the gas product quality and conversion efficiency. Process modifications by two-stage gasification and secondary air injection in the gasifier are also useful for tar reduction (Narvaez et al., 1997). The catalysts are effective, commercially available and relatively cheap (Sutton et al., 2001).

Fernando et al. 2009, gasified cellulose in supercritical water, in the absence of heterogeneous catalytic effects, by using quartz reactors. They also report the first systematic study of the effects of temperature, cellulose loading, water density, and reaction time on the production of H_2 , CH_4 , CO, and CO_2 from supercritical water gasification. The results show that the total gas yields and H_2 mole fraction were lower in quartz reactors than in stainless steel reactors. These comparisons indicate that the reactor surface influences both the rate of gas formation and the composition of the gas. This outcome confirms that gases

formed in metal reactors arise from both homogeneous and heterogeneous reactions, even in the absence of an added catalyst. Therefore, one needs both the homogeneous and heterogeneous reaction kinetics for SCWG to properly design, scale up, or optimize an SCWG reactor. The rate of formation for all gas species increased with temperature. It also increased the mole fractions of H_2 and CH_4 in the gaseous products. Manipulating cellulose loading and water density provided an efficient means to control the product selectivity, since the relative amounts of H_2 and CH_4 were strongly influenced by these two process variables. In general, higher H_2 yields were obtained at the longer reaction times, higher water densities, higher cellulose loadings, and higher temperatures. In short, as the severity of the reaction conditions increased, the H_2 yield increased (Fernando et al., 2009).

As a summary there are some studies describing hydrothermal gasification of the lignin and a few studies for hemicellulose, which are forming 1/3 part of the biomass. Lignin is a complex high molecular weight compound with an even more random structure than hemicellulose. In plant cell walls, hemicellulose, together with lignin and cellulose, make up the lignocellulosic complex (Tokarzewska-Zadora, 2005). To elucidate the reaction pathways from phenolic and aromatic groups in lignin, it is important to study monomeric model compounds such as phenol and benzene. Yong et al. (2013) has investigated the effect of temperature and residence time on phenol and benzene decomposition in supercritical water at a pressure of 25 MPa. Under these conditions, they conclude that the composition of phenol and benzene was relatively slow. Phenol decomposition was faster than benzene. This study demonstrated the importance of the ring opening mechanism in further degrading aromatic and phenolic compounds into intermediates.

The gasification of cellulose, xylan, and lignin mixtures in supercritical water, at 673 K, 25 MPa, and a reaction time of 20 min were examined by Yoshida et al. Their results indicate that the lignin content significantly affects the amount and composition of the product gas and the reaction of intermediates from cellulose and xylan with lignin resulted in a decrease in H_2 production. A set of equations developed to estimate the amount and composition of the product gas accurately predicted the actual results using only the lignin fraction as a parameter. This confirmed the importance of the lignin fraction effect on

supercritical water gasification characteristics (Yoshida et al., 2001). For instance hardwood hemicelluloses contain mostly xylans, whereas softwood hemicelluloses contain mostly glucomannans (Himmel, 1993). In herbaceous crops and hardwoods, xylan is a hetero-polysaccharide that consists of a homopolymeric backbone of β -(1,4) linked to xylose residues, which is generally the most common structure in hemicellulose. As a result, xylan conversion is critical for utilization of important biomass feedstocks such as bagasse, corn stover, miscanthus, a source of biomass for the production of biofuel, and poplar (Joseph, 2010).

In addition to cellulose, hemicelluloses and lignin, all species of biomass contain extraneous components. They are typically in the order of 2-40% of dry weight, depending on species and, location in the lignocellulosic biomass. Extractives often play an important role in the utilization of biomass. There are studies for extractives by maltose, cellobiose, starch, saccharose and fructose.

In this study, the simultaneous effect of the high reaction temperature, high pressure and catalyst on the gas and liquid product distribution were investigated to determine the ideal conditions for hydrothermal gasification of hemicellulose and extractives. The deficiency in the literature was eliminated by clarifying the reaction mechanism and the attitude in the supercritical water of the hemicellulose and extractives. Xylose, arabinose and pectin as model compound for the hemicellulose, tannic acid, gallic acid, 1,2,3 trihidroksibenzene and 1,3,5 trihidroksibenzene for extractives were selected. Hydrothermal gasification was performed in a batch reactor system at temperature and pressure ranges of 400, 500 and 600°C and 20, 27.5, 35.0 and 42.5 MPa. Xylose, arabinose and tannic acid were studied at 400, 500 and 600°C in the presence of, K_2CO_3 , KOH, activated carbon-Ni and activated carbon-Ru. Gallic acid, 1,2,3 trihidroksibenzene, 1,3,5 trihidroksibenzene and pectin were studied at 400, 500 and 600°C in the presence of K_2CO_3 and KOH. Galacturonic acid results, that have been completed in the TUBITAK Project (Saglam, 2013), were used to compare with the pectin results. The influences of temperature, pressure and catalyst were examined in relation to the maximum yields of the H_2 and CH_4 gases and the liquid products of furfurals, aldehydes and carboxylic acids by gas and liquid chromatographic techniques.

4.0 EXPERIMENTAL APPARATUS AND PROCEDURE

4.1 EXPERIMENTAL

Supercritical water gasification studies were performed with selected model compounds for hemicellulose; xylose, arabinose and pectin. Tannic acid, 1,2,3 trihidroksibenzene (Pyrogallol), 3,4,5 trihydroxybenzoic acid (Gallic acid), 1,3,5 trihydroxybenzene (Phloroglucinol) for extractives. All materials that have used in the experiments were given in the Table 4.1.1 by purity values and brands.

Table 4.1.1 Materials used in the experiments.

Material	Purity (%)	Supplier
D-(+)-Xylose	98	Alfa Aesar
D-(-)-Arabinose	99	Alfa Aesar
Pectin (Pectin from citrus peel) (Galacturonic acid $\geq 74\%$)		Sigma Aldrich
Tannic acid ($C_{76}H_{52}O_{46}$)	99.5	Alfa Aesar
Gallic acid (3,4,5 Trihydroxybenzoic acid monohydrate) ($C_7H_6O_5 \cdot H_2O$)	99	Alfa Aesar
Pyrogallol ($C_6H_6O_3$)	98	Alfa Aesar
Phloroglucinol (Phloroglucinol dehydrate- $C_6H_6O_3 \cdot 2H_2O$)	98	Alfa Aesar

The activated carbon (Charcoal activated, Merck) was used as a support for nickel and ruthenium catalysts. Ni/AC and Ru/AC catalysts formulations have been studied by an incipient wetness method for the experiments. Nickel nitrate hexahydrate [$Ni(NO_3)_2 \cdot 6H_2O$] was used as precursor for the preparation of the Ni/AC, purchased from Merck. Ruthenium (III) chloride hydrate [$RuCl_3 \cdot xH_2O$] was used as precursor for the preparation of the Ru/AC, purchased from Sigma Aldrich. The catalysts were calcined in a nitrogen flow at 500°C for 3h. Ni and Ru loading were 5 wt% in the activated carbons. Both fresh and spent catalysts (AC,

Ni/AC and Ru/C) were characterized to obtain information on the surface area, total pore volume and the surface morphologies. The BET surface area and total pore volume were measured by N₂ physical adsorption using Micromeritics Gemini V model. The materials were degassed under vacuum at 300°C for 3 h prior to nitrogen adsorption. Morphology of the catalysts were observed by SEM system (FEI Quanta 250 FEG).

Supercritical water gasification experiments were carried out in a high temperature (maximum temperature of 650°C) and high pressure (maximum pressure of 50 MPa) in the stainless steel batch reactor (SS316). Figure 4.1.1 shows the experimental setup employed in this study. Figure 4.1.2 shows the heater and autoclave batch system. Depending on the requirements of the analytical method applied, analytically pure or HPLC pure reagents were used. The temperature and pressure were controlled by the analogue manometer and thermocouple. Mixing was achieved by a motor-driven tumbling movement.

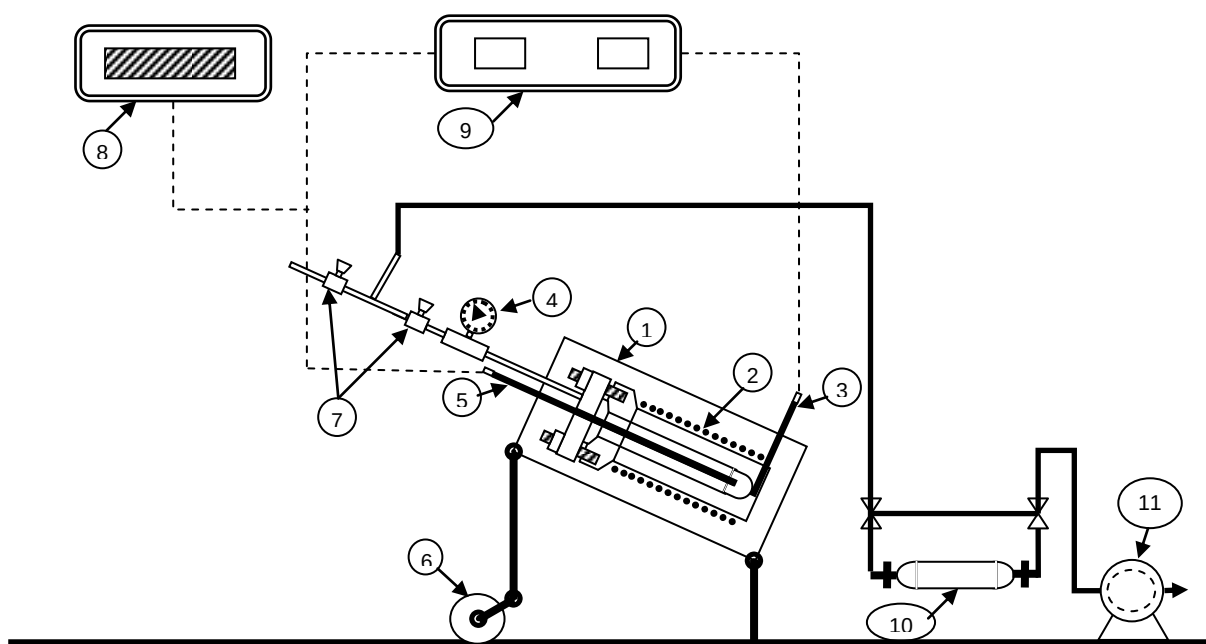


Figure 4.1.1 Schematic diagram of the SCWG system; 1, autoclave; 2, electrical heater; 3, outside thermocouple; 4, pressure gauge; 5, inner thermocouple; 6, rotating shaker with an eccentric; 7, high pressure valves; 8, recorder; 9, PID controller; 10, gas sample outlet; 11, gasometer.



Figure 4.1.2 Heater and autoclave batch system.

Desired amount of substance and water (1.2 g of substance/15 mL of water) was placed into autoclave. The amount of water was determined by preliminary tests so that desired four pressures (20, 27.5, 35 and 42.5 MPa) for the operating temperatures 400, 500 and 600°C were attained. A total of 0.55-3.5 g substance and 10 wt.% K_2CO_3 were well mixed and loaded into the reactor with water. All experiments were performed in triplicate with a resulting precision of product yields about 5%. After loading, the autoclave is flushed by nitrogen to remove air in the reactor. Operating pressure was reached at the set temperature of the experiment. After the reaction time (1h), the reactor was immediately immersed in a water bath to terminate the reaction and allowed to reach the ambient temperature. After the reactor had been cooled, the amount of product gas was measured by a gasometer after expansion to ambient pressure and gas samples were taken using for analysis by a gas chromatography. The gas volume was measured in $\pm 10\%$ accuracy. Figure 4.1.3 shows a schematic diagram of the experimental procedure employed for the products.

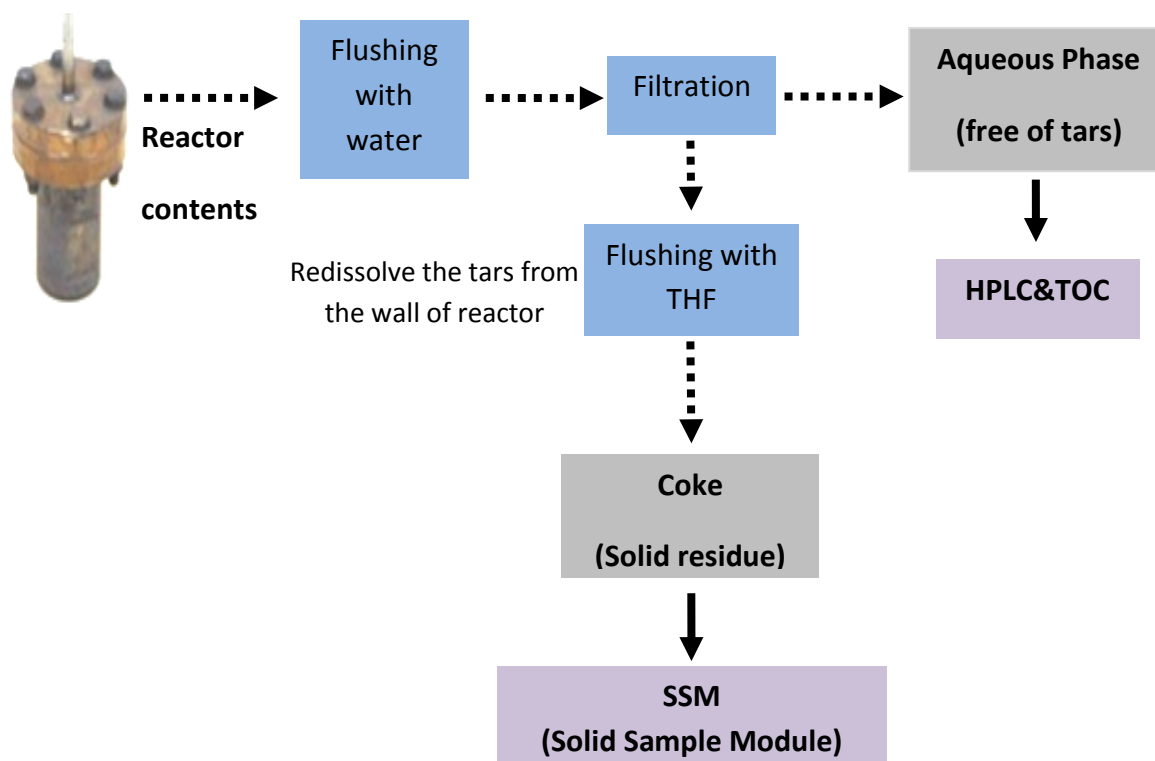


Figure 4.1.3 Experimental procedure for the analysis of the products.

The products remaining in the reactor were washed with water and filtered to separate solid residue. Sticky brown humin polymers were observed at temperatures lower than 450°C in the reactor. After removal of the products in the reactor, the inside of reactor was washed with THF (tetrahydrofuran). THF was evaporated under vacuum by using a rotary evaporator and the amount of this product (tar) was found extremely low compared with the filtrated solid (char). Total of char and tar were called as residue. pH of aqueous products was lowered to 2 by addition of 1–2 drops of concentrated sulphuric acid which was required to inhibit ionization of organic acids.

4.2 ANALYSES

Analysis of biomass and SCWG products (aqueous, gaseous and solid residue) were conducted by using equipments below (Table 4.2.1).

- GC: Agilent Gas Chromatography (Model: 7890 A)
- HPLC: Shimadzu Liquid Chromatography System (Model: LC-20A)
- HPLC: Agilent Liquid Chromatography System (Model: 1200 Series)
- TOC: Shimadzu total organic carbon analyser (Model: TOC-VCPH, Solid Sample Module: SSM-5000A)
- Colorimeter: Jenway Colorimeter (Model: 6051)

Table 4.2.1 Equipments used in analyses of biomass and SCWG products.

Products	Compounds	Equipment
Gaseous	CO, CO ₂ , H ₂ , CH ₄ ve C ₂ -C ₄ hydrocarbons	Gas Chromatography
Aqueous	Phenol and its derivatives	Colorimeter
	Organic acids, phenols and fufurals	HPLC with UV-VIS detector
	Alcohols and sugars	HPLC with RI detector
	Total organic carbon	TOC
Solid residue and biomass	Total organic carbon	TOC-SSM

4.2.1 Gas Phase Analysis

The gaseous products were analyzed using a gas chromatography (HP 7890A, Wilmington–USA, Figure 4.2.1.1) was equipped with two thermal conductivity detectors (TCD) and a flame ionization detector (FID). Technical features and operating conditions of the gas chromatography were given in the Table 4.2.1.1. The columns used were of the type Hayesep Q, Molsieve 5A and HP-Plot Al_2O_3 S columns. Gas analysis was performed using helium carrier gas with a column temperature starting at 60°C. The GC oven temperature was held at 60°C for 1 min., then ramped to 80°C at a rate of 20°C/min, and ramped to 120°C at a rate of 30°C/min and finally held at 120°C for 2.66 min. The concentration of the gas species were taken as an average of the two injections. The standard deviation is typically less than 2% of the reported value. Gas products were identified by retention time and quantified by external calibration against the standard gas mixture.



Figure 4.2.1.1 Gas analysis system (Gas chromatography (HP 7890A, Wilmington–USA))

Table 4.2.1.1 Technical features and operating conditions of HP GC 7890A gas chromatography

Columns		Column 1 = Hayesep Q 80/100 mesh (0.5m x 1/8") Column 2 = Hayesep Q 80/100 mesh (6ft x 1/8") Column 3 = Molsieve 5A 80/100 mesh (8ft x 1/8") Column 4 = Hayesep Q 80/100 mesh (3ft x 1/8") Column 5 = Molsieve 5A 80/100 mesh (8ft x 1/8") Column 6 = DB-1 (pre-column) Column 7 = HP-Plot Al ₂ O ₃ S(25m x 0.32mm x 8μ)
Oven Program	Temperature	60°C isothermal for 1 min. 20°C/min. to 80°C 30°C/min. to 120°C isothermal for 2.66 min.
Mobile phase		Helium
Operating mode		Split (Ratio= 80:1, Flow= 60 mL/min)
Injection Temperature		250 °C
Detector Temperature		Front signal – FID- 250°C Back signal – TCD- 250°C Auxiliary signal – TCD- 250°C

4.2.2 Liquid Phase Analysis

Determinations of the aqueous phase (carboxylic acids, phenols, aldehydes, furfurals and ketones) were made by the HPLC method with the use of Shimadzu LC-20A series liquid chromatography, equipped with an Inertsil ODS-4 (250 mm long×4.6 mm i.d) column. The HPLC system consist of a DGU-20AS degassing module, LC-20AT gradient pump, CTO-10ASVP chromatography oven and SPD-20 multi-wavelength ultraviolet detector (Figure 4.2.2.1). Organic acids, phenols and furfurals were analysed with Method I (Table 4.2.2.1) and aldehydes were analysed with Method II (Table 4.2.2.2). As the mobile phase we used a solution composed of phosphoric acid (0.05 vol.% H₃PO₄) and a solution [acetonitrile (CH₃CN)/water (H₂O)] at the 80:20 v/v ratio to analyze carboxylic

acids, phenols and furfurals. The mobile phase flow rate was 1 mL min^{-1} , while the components were determined at different wavelengths of 232-290 nm.

The aldehydes and ketones were derivatized to their hydrozone forms by addition of 2,4-dinitrophenylhydrazine into aqueous samples to analyze by high-performance liquid chromatography as the same method described in the literature (Nascimento, 1997). With the use of the mobile phases water and methanol, the aldehydes and ketones were analyzed by applying at a flow rate of 1 mL min^{-1} , while the components were determined at different wavelengths of 365 nm. Technical features and operating conditions of HPLC for Method II was given in the Table 4.2.2.2. HPLC Standards Analysed by Method I and Method II were given in the Table 4.2.2.3. The amounts of different phenols were determined colorimetrically by a colorimeter (Jenway model 6051).

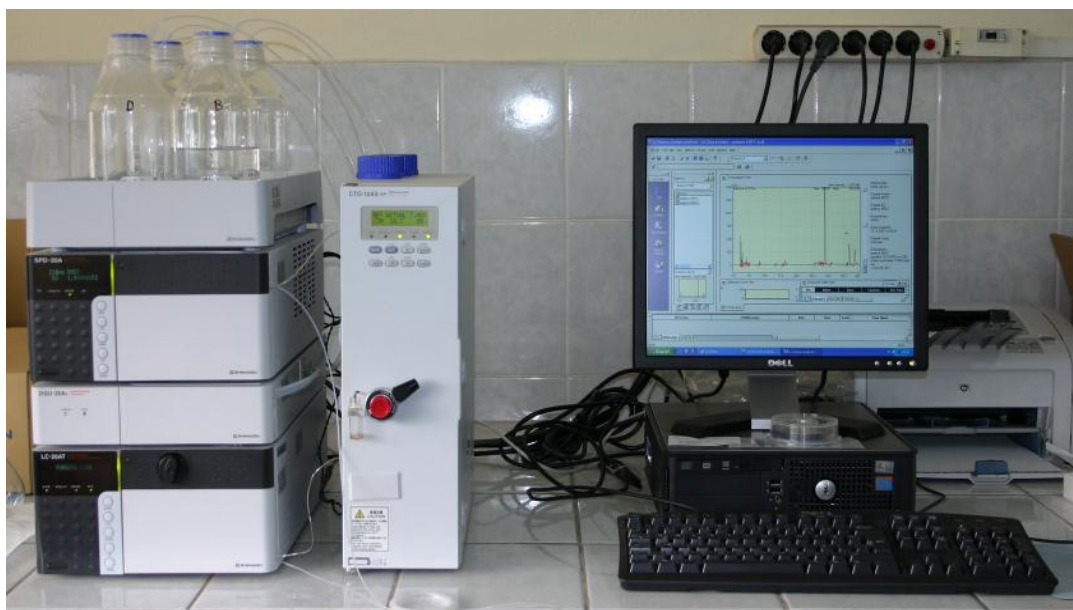


Figure 4.2.2.1 HPLC system (Shimadzu LC-20A series liquid chromatography)

Table 4.2.2.1 Technical features and operating conditions of HPLC for Method I

Column	Intersil ODS-4 (250 mm length x 4.6 I.D.)
Mobile Phase	A: 0.05 % vol. H ₃ PO ₄ (pH: 2.25) – B: CH ₃ CN/H ₂ O (90/10: vol/vol.)
Flowrate	1 mL/min
Detector	UV
Wavelength	210 nm
Column temperature	30°C
Detector temperature	30°C
Injection volume	20 µL
Low temperature gradient program of mobile phase	1. min. 90% A ve 10% B 17. min. 90% A ve 10% B 25. min. 65% A ve 35% B 35. min. 65% A ve 35% B

Table 4.2.2.2 Technical features and operating conditions of HPLC for Method II

Column	Intersil ODS-3 (250 mm length x 4.6 I.D.)
Mobile Phase	A: Water B: Methanol
Flowrate	1 mL/min
Detector	UV
Wavelength	365 nm
Column temperature	30°C
Detector temperature	30°C
Injection volume	20 µL
Low temperature gradient program of mobile phase	1. min. 35% A ve 65% B 5. min. 35% A ve 65% B 15. min. 15% A ve 85% B 35. min. 10% A ve 90% B 45. min. 10% A ve 90% B

Table 4.2.2.3 HPLC Standards Analysed by Method I and Method II were given below.

Standards Analysed by Method I	Standards Analysed by Method II
• Formic acid • Acetic acid • 5-methylfurfural • 1,4 dioxan • Furfural • 3-methyl-2 cyclopentan-1-on • Phenol • o- cresol • m- cresol • p-cresol	• Formaldehyde • Acetaldehyde • 5-methylfurfural • 1,4 hydroxy dioxan • Furfural • 3-methyl-2 cyclopentan-1-on • Acetone • Methyl ethyl ketone • Hydroxyacetic acid

4.2.2.1 HPLC Analysis of Aldehydes with Method II

Reagents:

The standard aldehydes were of analytical grade (Merck, Aldrich). Methanol and acetonitrile were of HPLC grade (Merck). Water was distilled using a Milli-Q system (Millipore). 2,4- Dinitrophenylhydrazine (BDH) was purified by three successive recrystallizations from methanol.

Preparation of 2,4 -dinitrophenylhydrazones of the standard aldehydes:

2,4-dinitrophenylhydrazine (0.4 g; ca. 2 mmol) was dissolved in concentrated sulfuric acid (2 mL) and distilled water (3 mL). To this solution, the standard aldehydes (0.1 g), dissolved in ethanol (15 mL), were added. The corresponding aldehyde-DNPHs were isolated via filtration and purified (twice) by recrystallization from absolute ethanol.

Sample derivatization:

A 0.4% solution of 2,4-dinitrophenylhydrazine was prepared by dissolving 2,4-dinitrophenylhydrazine (0.4 g; ca. 2 mmol) in acetonitrile (100 mL). In a volumetric flask, 1.0 mL of the 2,4-dinitrophenylhydrazine solution, 4.0 mL of the sample (without previous concentration) and 50 μL of 1 M HClO_4 were introduced, consecutively. The resulting solution was stirred at room temperature for at least 45 min, and then mixed with 2 mL of acetonitrile followed by syringe.

4.2.3 Analysis of Solid Residue and Sample

Analysis of solid residue was performed with TOC-SSM (Shimadzu TOC- V_{CPH} -SSM-5000A, Japan, Figure 4.2.3.1). Calibration of TC (Total Carbon) unit renewed by using sucrose as standard.



Figure 4.2.3.1 Total organic carbon analysis system (Shimadzu TOC- V_{CPH} -SSM-5000A, Japan).

5.0 EVALUATION OF RESULTS

In this study, hydrothermal gasification of xylose, arabinose and pectin as model compound for the main polysaccharide in hemicellulose, tannic acid, gallic acid, 1,2,3 trihidroksibenzene and 1,3,5 trihidroksibenzene for extractives were carried out at high temperatures (400, 500 and 600°C) and high pressures (20, 27.5, 35.0 and 42.5 MPa with a constant reaction time. Experiments were performed without and with adding 10 wt% of catalyst. The experimental plan of this study was given in the Table 5.1. Xylose, arabinose and tannic acid were studied at 400, 500 and 600°C in the presence of KOH, activated carbon-Ni and activated carbon-Ru. Gallic acid, 1,2,3 trihidroksibenzene, 1,3,5 trihidroksibenzene and pectin were studied at 400, 500 and 600°C in the presence of K_2CO_3 and KOH. Total of 268 hydrothermal gasification experiments were performed in a batch reactor system. Xylose and arabinose studies were completed in the TUBITAK Project 109M284 (Sağlam, 2013). Galacturonic acid results, that have been completed in the TUBITAK Project (Sağlam, 2013), were used to compare with the pectin results. Since the experiments were repeated at least three times, the average yield was able to evaluate and the reproducibility confirm.

In the experimental test, it is concluded that the reaction time of 1 hour is sufficient to reach the maximum conversion at the lowest typical supercritical water gasification temperature under the noncatalytic condition. Also in the presence of typical Ni and Ru catalysts, the hydrogen yield decreases due to methanation reaction, so that it is not possible to increase the hydrogen yield simply by extending the reaction time (Azadi et al., 2012). The influences of temperature, pressure and catalyst were examined in relation to the maximum yields of the H_2 and CH_4 gases and the liquid products of carboxylic acids, furfurals, aldehydes and ketones by gas and liquid chromatographic techniques. The comparison of the experimental results, such as the volume of the gas phase, composition of the gas and the liquid products together with total organic carbon content (TOC) provide knowledge of the chemical reaction pathways of the model compounds and their dependence on the reaction conditions, temperature, pressure and catalyst. Contributions of this study to literature in this field are diversity of model compound that represent hemicelluloses and extractives fractions of lignocellulosic biomass and type of catalysts used.

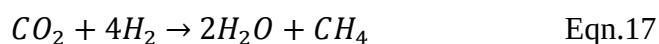
Table 5.1 Experimental Plan

Exp. Number	Catalyst type Material	Reaction Conditions	Without catalyst	K ₂ CO ₃	KOH	AC-Ni	AC-Ru
1-20	Xylose	300, 400, 500 and 600°C					
101-124		400, 500 and 600°C 200, 275, 350 and 425 atm					
21-40	Arabinose	300, 400, 500 and 600°C					
125-148		400, 500 and 600°C 200, 275, 350 and 425 atm					
41-55	Tannic acid	400, 500 and 600°C					
149-172		400, 500 and 600°C 200, 275, 350 and 425 atm					
56-64	Gallic acid (3,4,5 trihydroxybenzoic acid)	400, 500 and 600°C					
173-196		400, 500 and 600°C 200, 275, 350 and 425 atm					
65-73	Phloroglucinol) (1,3,5 trihydroxybenzene)	400, 500 and 600°C					
197-220		400, 500 and 600°C 200, 275, 350 and 425 atm					
74-82	Pyrogallol (1, 2, 3 trihydroxybenzene)	400, 500 and 600°C					
221-244		400, 500 and 600°C 200, 275, 350 and 425 atm					
83-91	Pectin	300, 400, 500 and 600°C					
245-268		400, 500 and 600°C 200, 275, 350 and 425 atm					
92-100	Galacturonic acid	300, 400, 500 and 600°C					

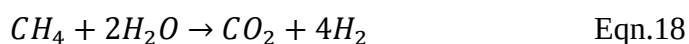
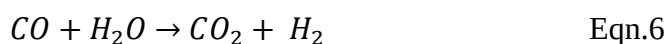
5.1 Influence of Temperature and Catalyst on the Product Distribution and Gas Composition

For the calculation of the carbon recovery of the experiments, carbon amount measured in all phases and carbon balance of products were kept within 95–99%. Yield values for the products are calculated by the ratio of carbon amounts in the gas, liquid products and residue (tar+char) to the total carbon amounts in xylose. In the appendices part, Tables 1-19 display the experimental results for supercritical water gasification of xylose, arabinose, tannic acid, gallic acid, phloroglucinol, pyrogallol, pectin and galacturonic acid at different temperatures (300 to 600°C) and catalyst. The table presents the normalized gas product distribution in mole percent after the removal of nitrogen purge gas from the analyses results. The product distribution and products composition are strongly affected by the reaction temperature and catalyst. Reaction temperature is the most important parameter that influences the gas composition. Temperature and catalyst effects on gas product yields of the selected model compounds; xylose-arabinose, tannic acid-gallic acid, phloroglucinol-pyrogallol and pectin-galacturonic acid hydrothermal gasification were given in the Figures 5.1.1-5.1.4, respectively as comparable. Gasification efficiency is increased sharply with temperature while liquefaction, residue amount and TOC in liquid product reduced with it. Temperature and catalyst effects on coke yields of the selected model compounds; xylose-arabinose, tannic acid-gallic acid, phloroglucinol-pyrogallol and pectin-galacturonic acid hydrothermal gasification were given in the Figures 5.1.21-5.1.24, respectively. The highest gas products and the lowest residue amounts were obtained at 600°C in the presence of K_2CO_3 or KOH. Temperature and catalyst effects on TOC yields of the selected model compounds; xylose-arabinose, tannic acid-gallic acid, phloroglucinol-pyrogallol and pectin-galacturonic acid hydrothermal gasification were given in the Figures 5.1.24-5.1.28, respectively. Alkali catalysts promoted sugar degradation while inhibiting the char formation, increase hydrogen and decrease CO yield by acceleration of the water gas shift reaction (Elliott 2004, Matsumura 2005). AC-Ni and AC-Ru had also similar effect under the same reaction conditions. The catalytic effects of K_2CO_3 and KOH was explained by catalysis water-gas shift reaction via the formate formation ($HCOO^-K^+$) in the Equations 6 to 10.

In all reaction cases, the gaseous product was composed of hydrogen, carbon dioxide, methane carbon monoxide as major components and ethane, ethene, propane, and propene as minors. C4- and higher hydrocarbons were not detected. Temperature and catalyst effects on hydrogen yields of the selected model compounds; xylose-arabinose, tannic acid-gallic acid, phloroglucinol-pyrogallol and pectin-galacturonic acid hydrothermal gasification were given in the Figures 5.1.5-5.1.8, respectively. Although catalyst effect for the high temperature gasification is not favorable, the selectivity in the gas products and the activation energy for biomass gasification reaction increases at high temperatures (Goodwin et al., 2006). The hydrothermal gasification experiments of the selected model compounds showed that H₂ selectivity increases slightly when catalysts were used for the reaction temperatures 400, 500 and 600°C. The concentration of CH₄ was increased as reaction temperature was raised from 400 to 600°C. Temperature and catalyst effects on methane yields of the selected model compounds; xylose-arabinose, tannic acid-gallic acid, phloroglucinol-pyrogallol and pectin-galacturonic acid hydrothermal gasification were given in the Figures 5.1.9-5.1.12, respectively as comparable. CH₄ in the product gas is produced from i.e. the methanation, and hydrogasification reactions and from reactions of organic liquid intermediates (Goodwin 2010, Resende 2008). Minowa et al. suggested that decreased H₂ production inhibited the methanation reaction by methanation of CO (Eq.(1)) and also by CO₂ (Eq.(2) (Minowa 1995).



For reaction temperatures of 600°C and lower, the majority of the product gas is comprised of H₂ and CO₂, also the product gas contained significant amount of CH₄. Temperature and catalyst effects on CO₂ yields of the selected model compounds; xylose-arabinose, tannic acid-gallic acid, phloroglucinol-pyrogallol and pectin-galacturonic acid hydrothermal gasification were given in the Figures 5.1.13-5.1.16, respectively. An decrease in the concentration of CO was observed as reaction temperature increased. CO₂ production highly catalyzed with water gas shift reaction (Eqn.6), and/or methane steam reforming (Eqn.18):



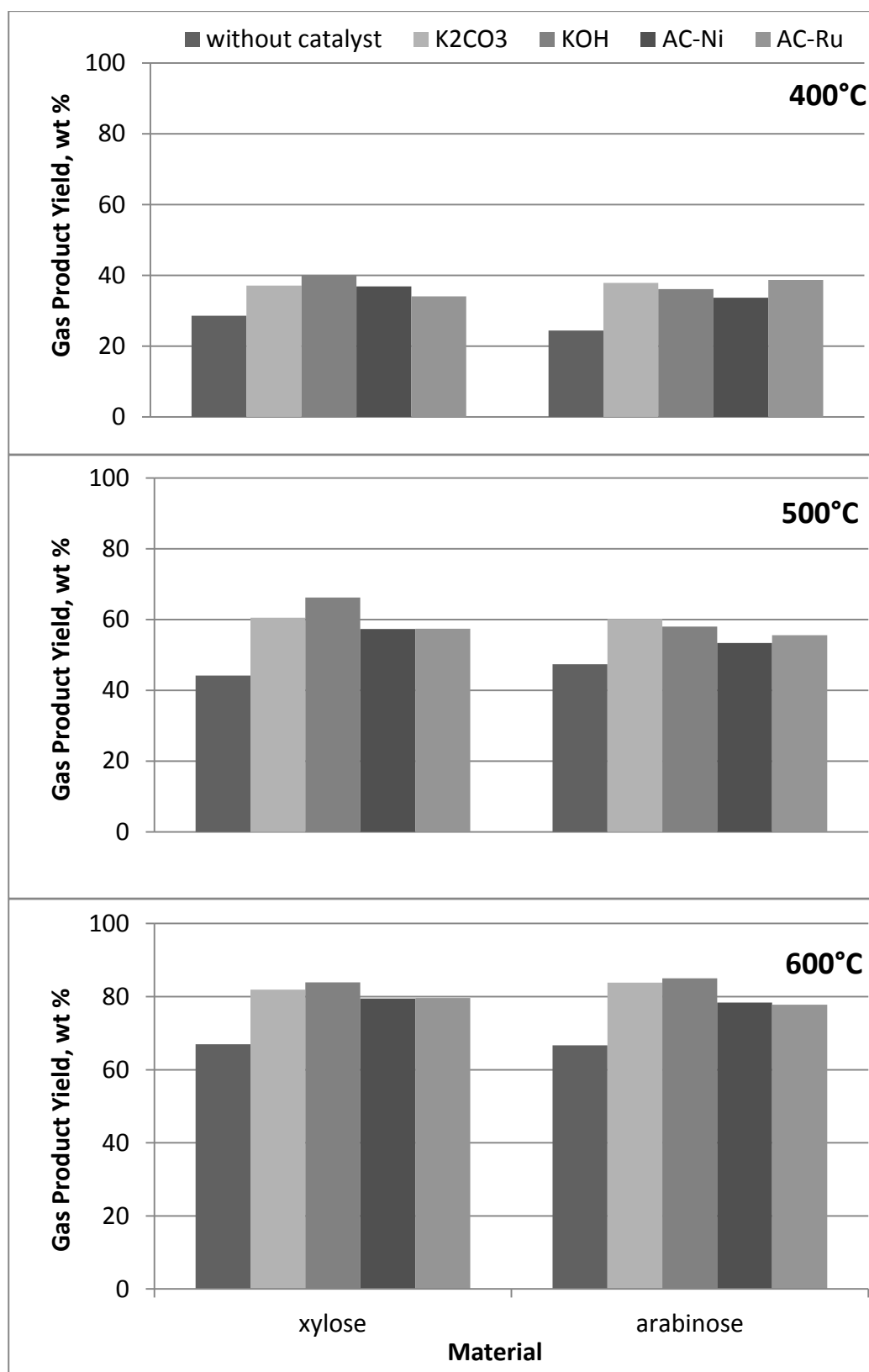


Figure 5.1.1 Temperature and catalyst effects on gas product yields of xylose and arabinose hydrothermal gasification.

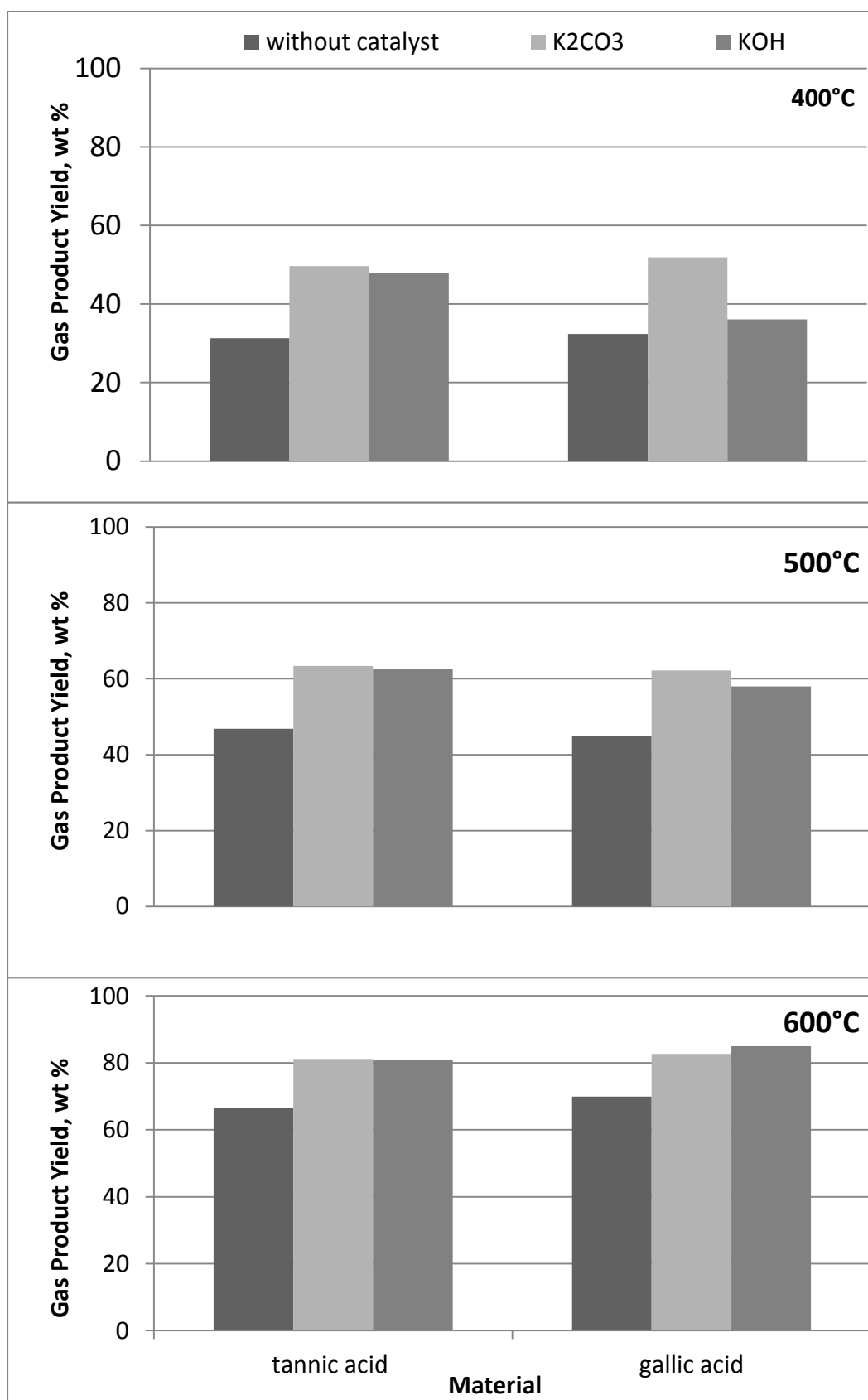


Figure 5.1.2 Temperature and catalyst effects on gas product yields of tannic acid and gallic acid.

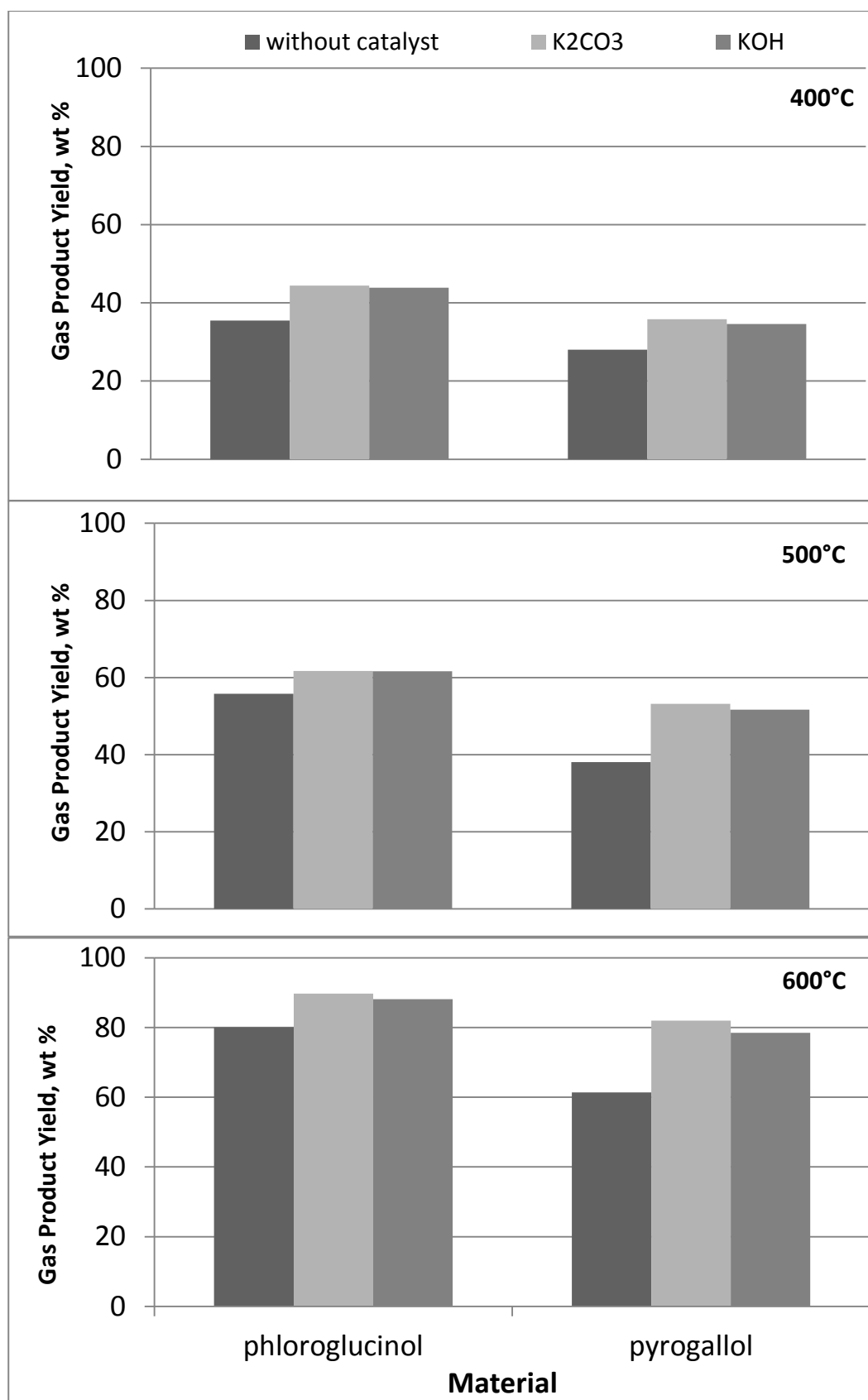


Figure 5.1.3 Temperature and catalyst effects on gas product yields of phloroglucinol and pyrogallol.

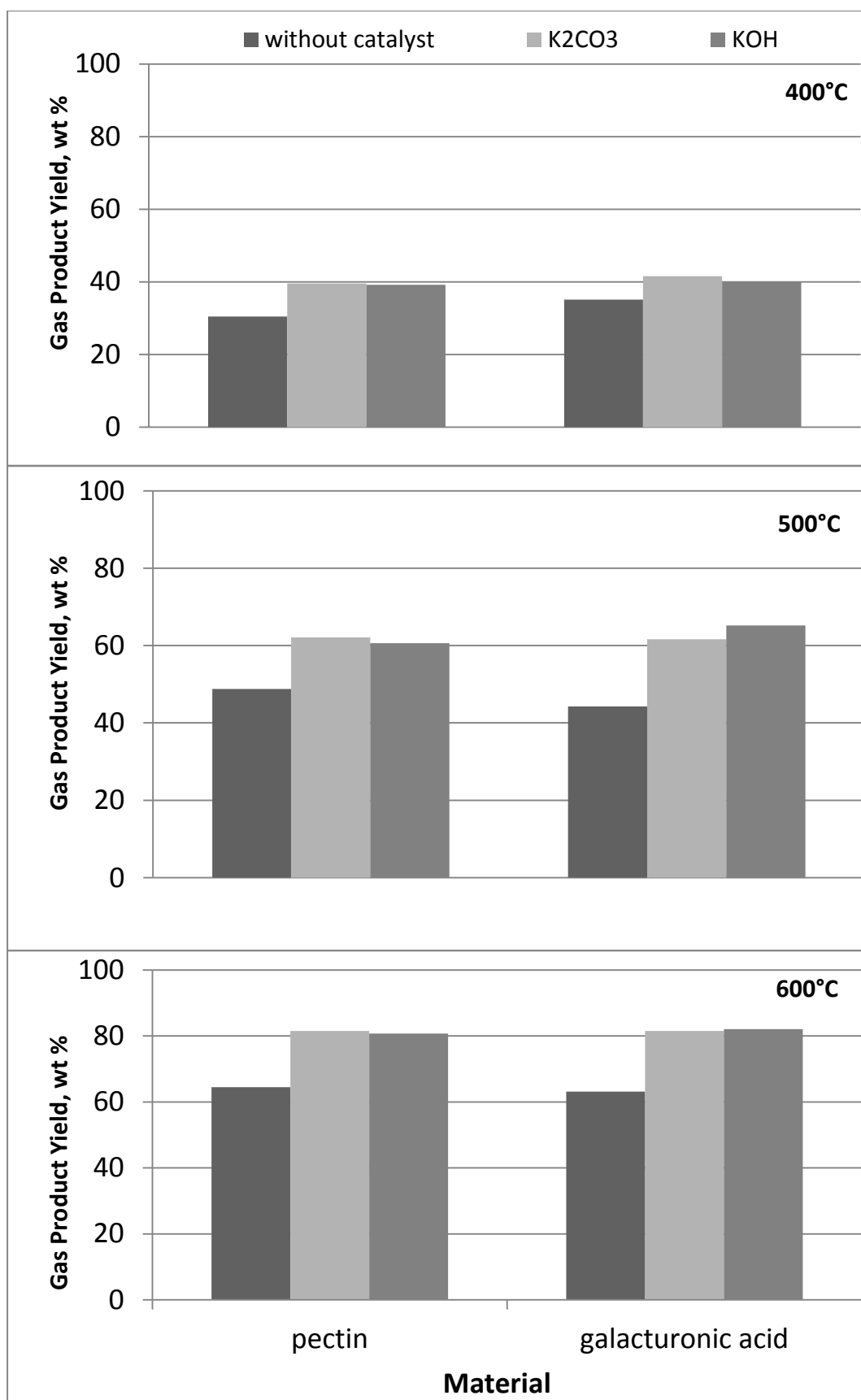


Figure 5.1.4 Temperature and catalyst effects on gas product yields of pectin and galacturonic acid hydrothermal gasification.

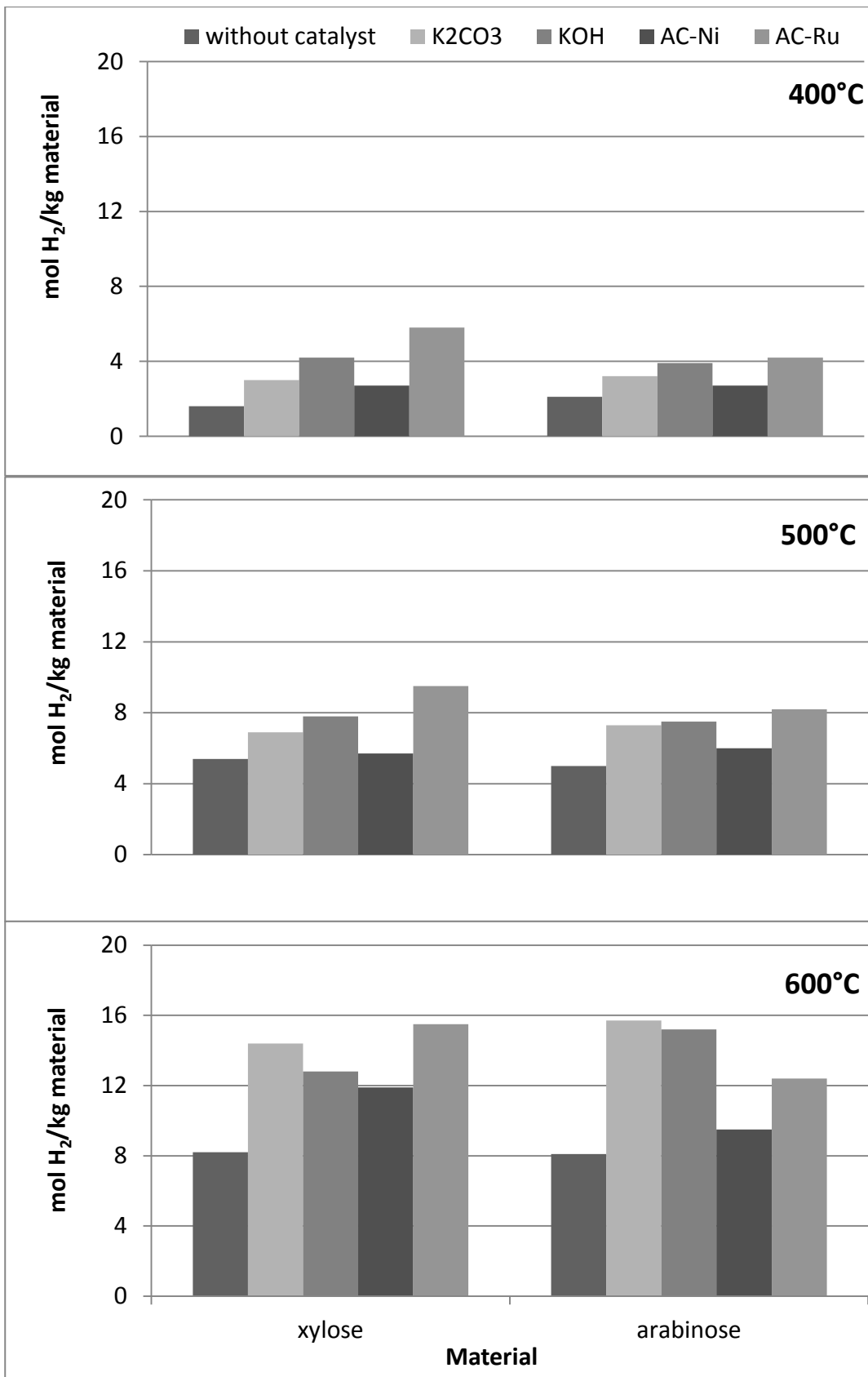


Figure 5.1.5 Temperature and catalyst effects on hydrogen yields of xylose and arabinose hydrothermal gasification.

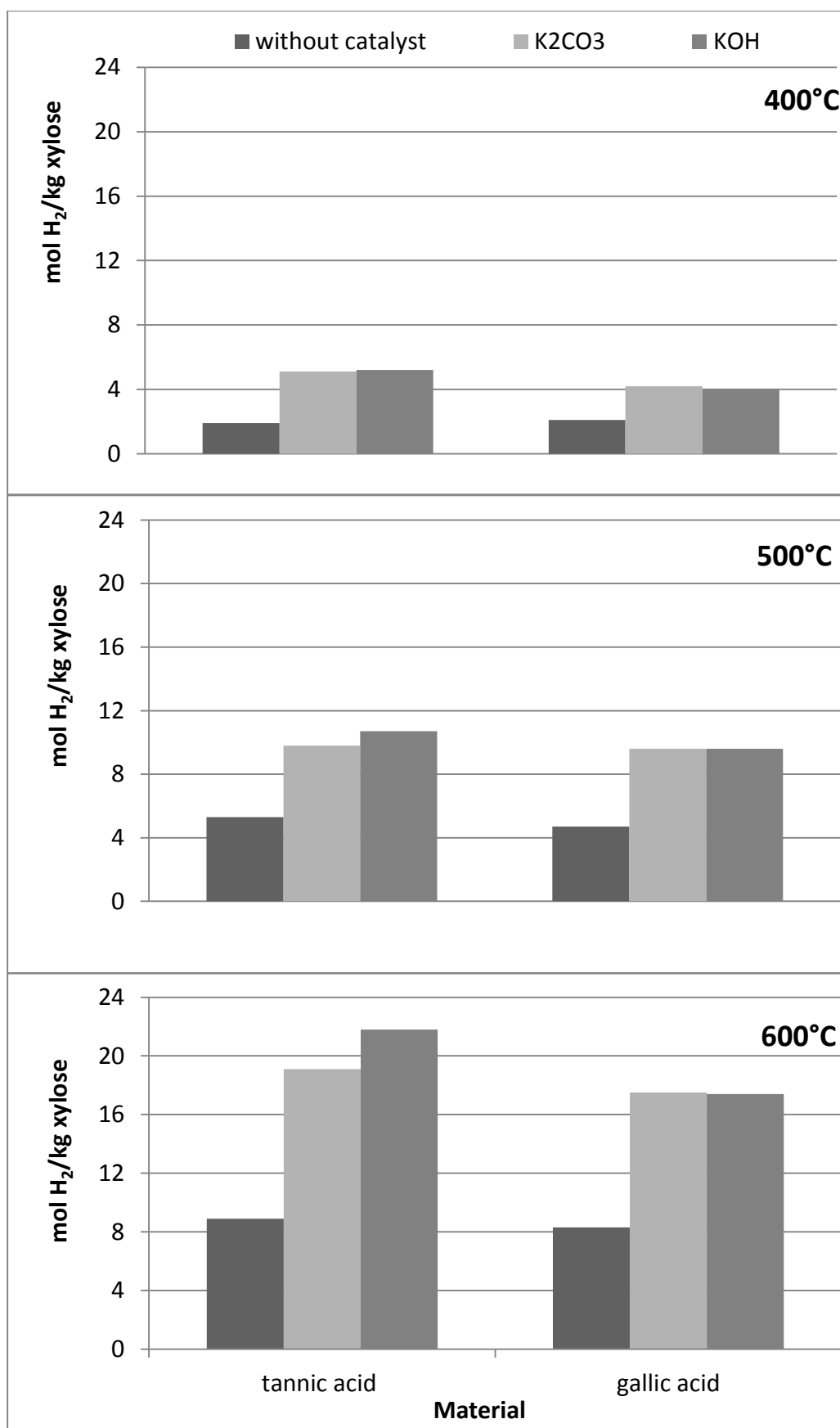


Figure 5.1.6 Temperature and catalyst effects on hydrogen yields of tannic acid and gallic acid.

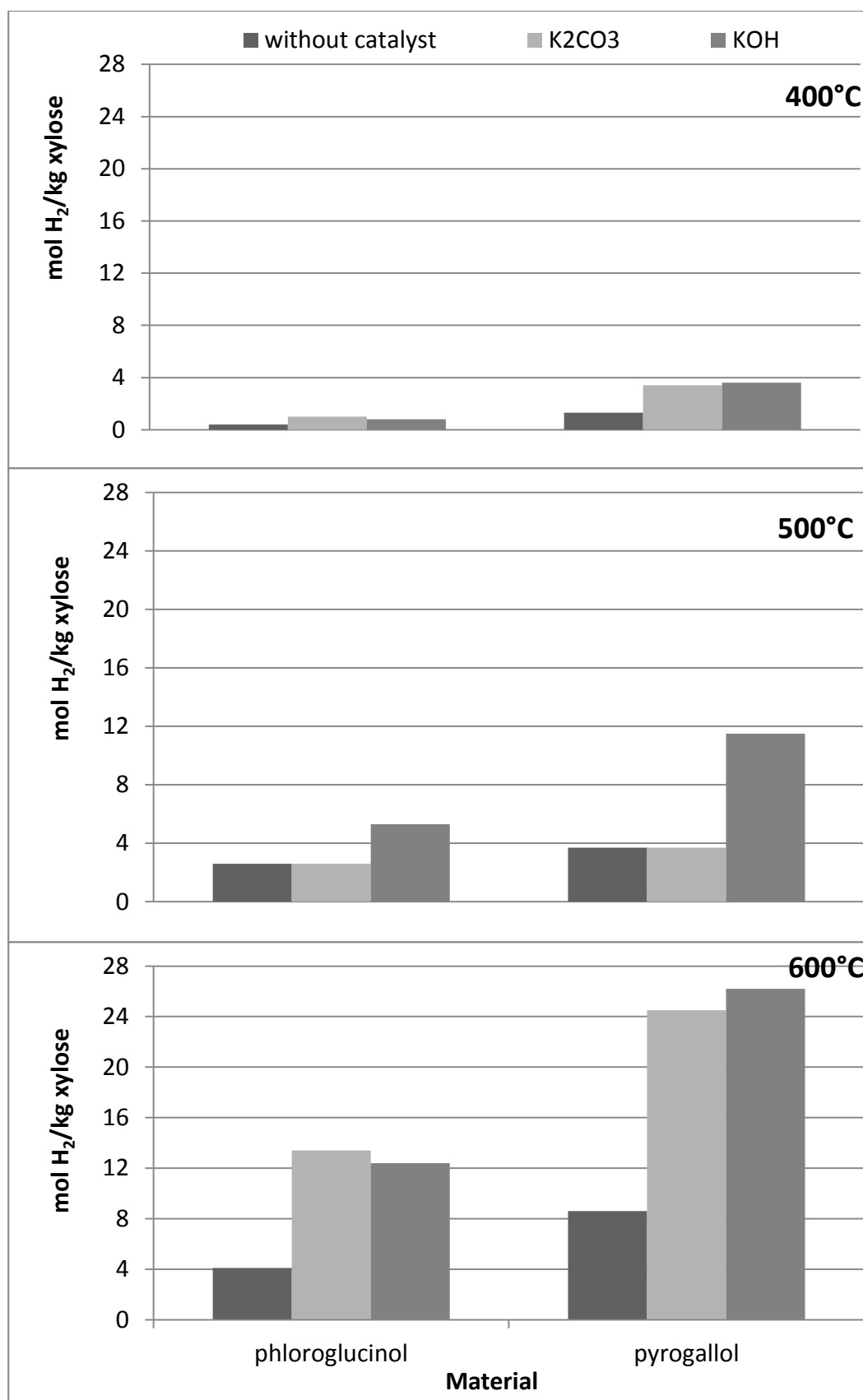


Figure 5.1.7 Temperature and catalyst effects on hydrogen yields of phloroglucinol and pyrogallol.

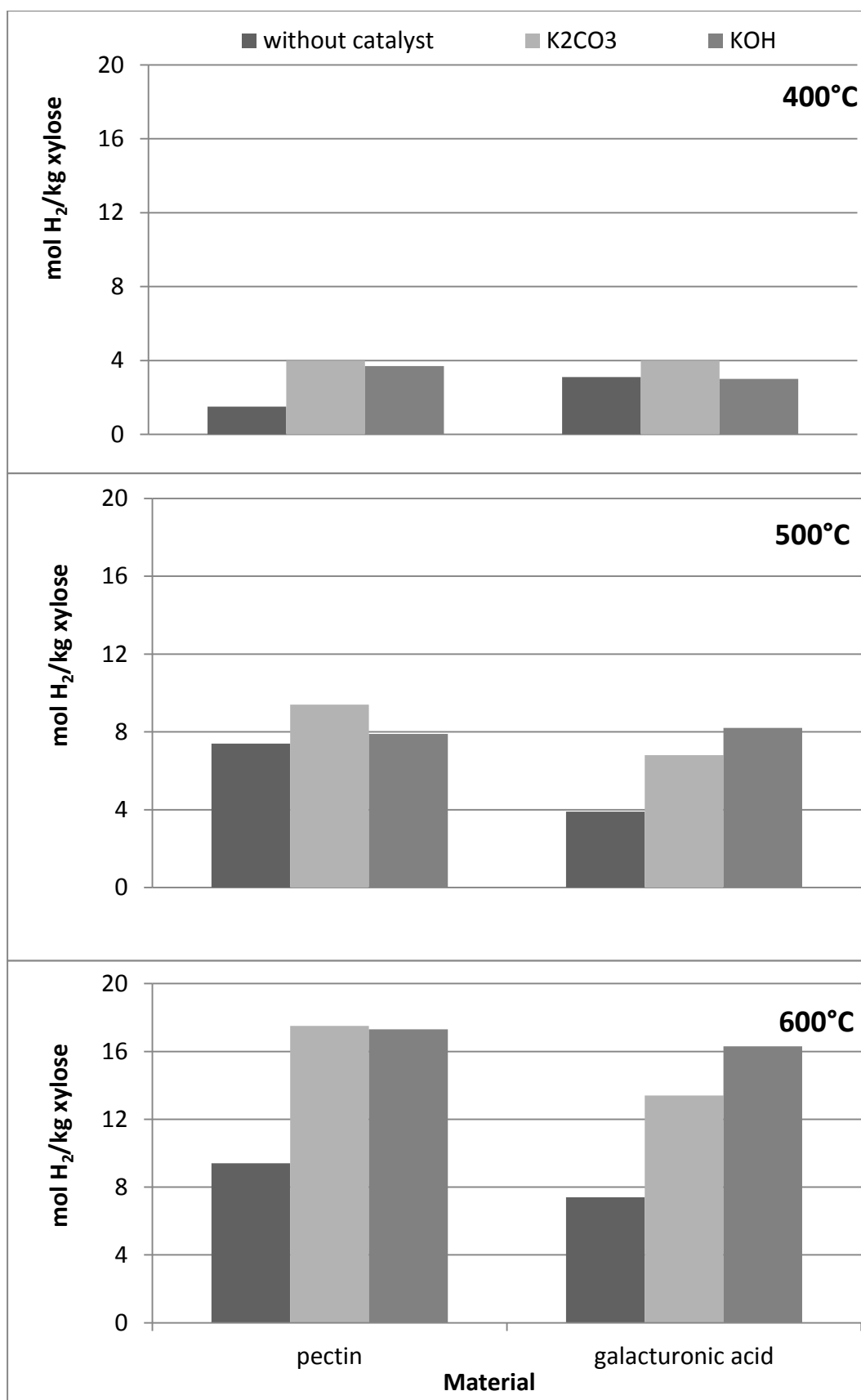


Figure 5.1.8 Temperature and catalyst effects on hydrogen yields of pectin and galacturonic acid hydrothermal gasification.

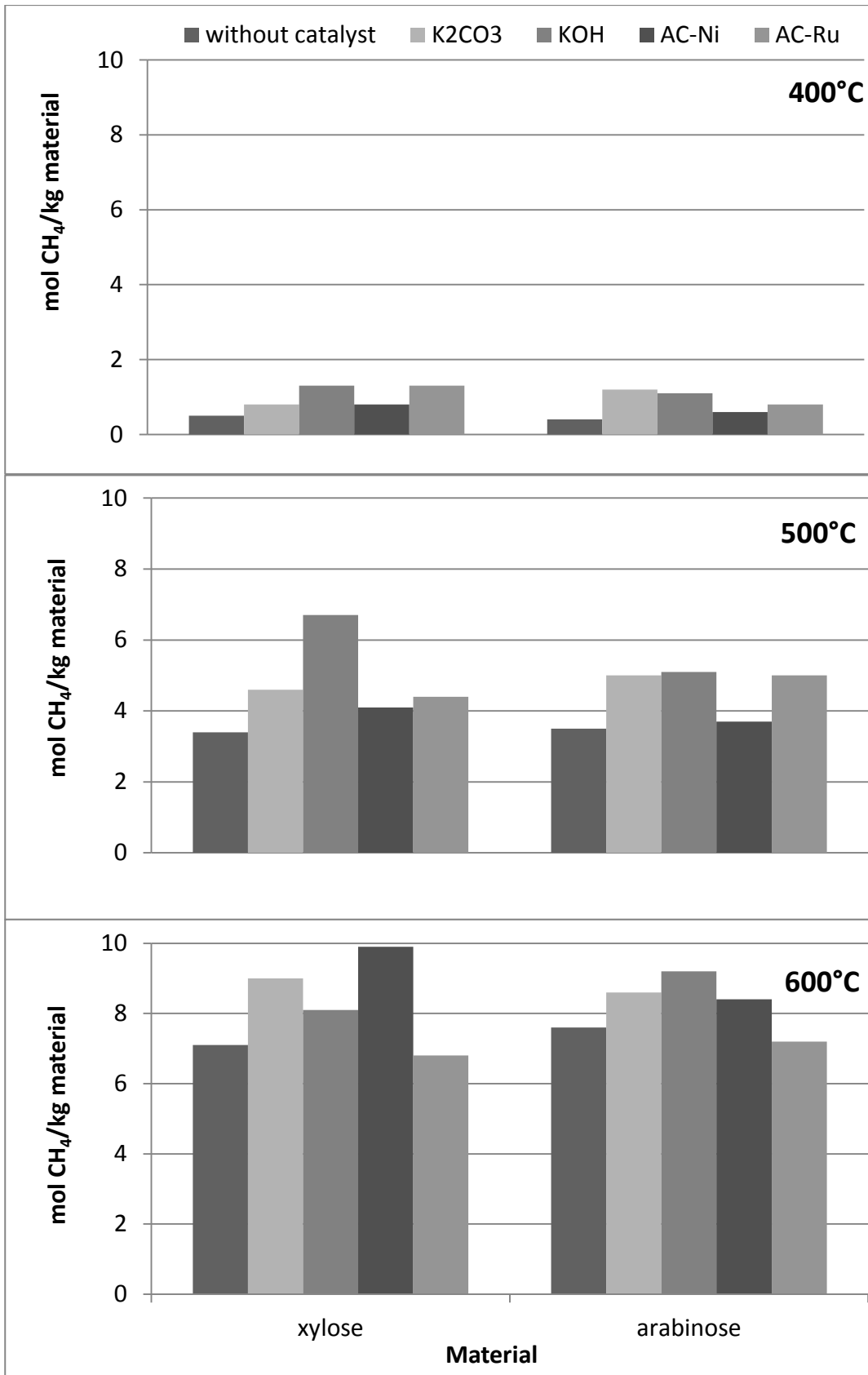


Figure 5.1.9 Temperature and catalyst effects on methane yields of xylose and arabinose hydrothermal gasification.

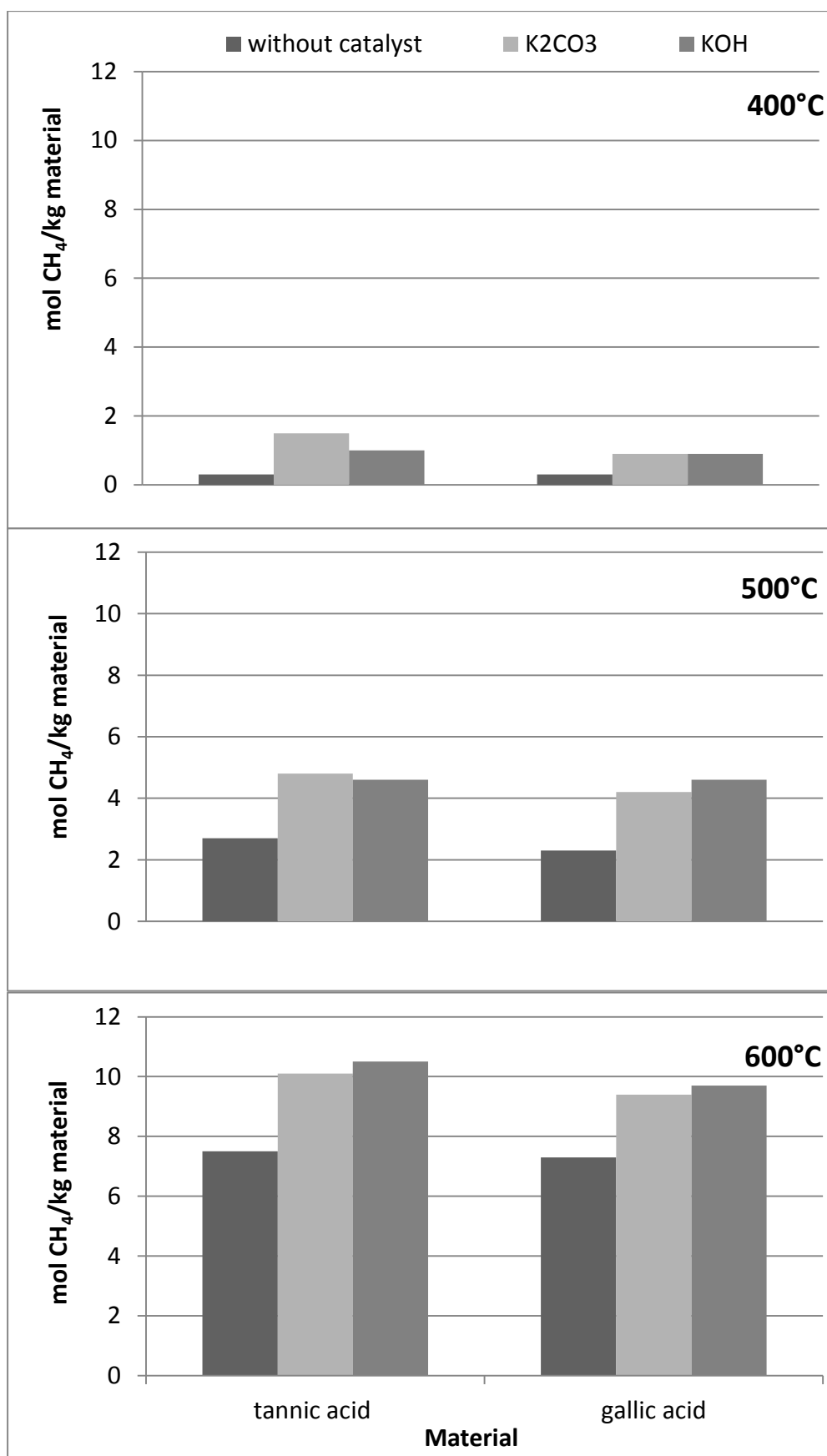


Figure 5.1.10 Temperature and catalyst effects on methane yields of tannic acid and gallic acid.

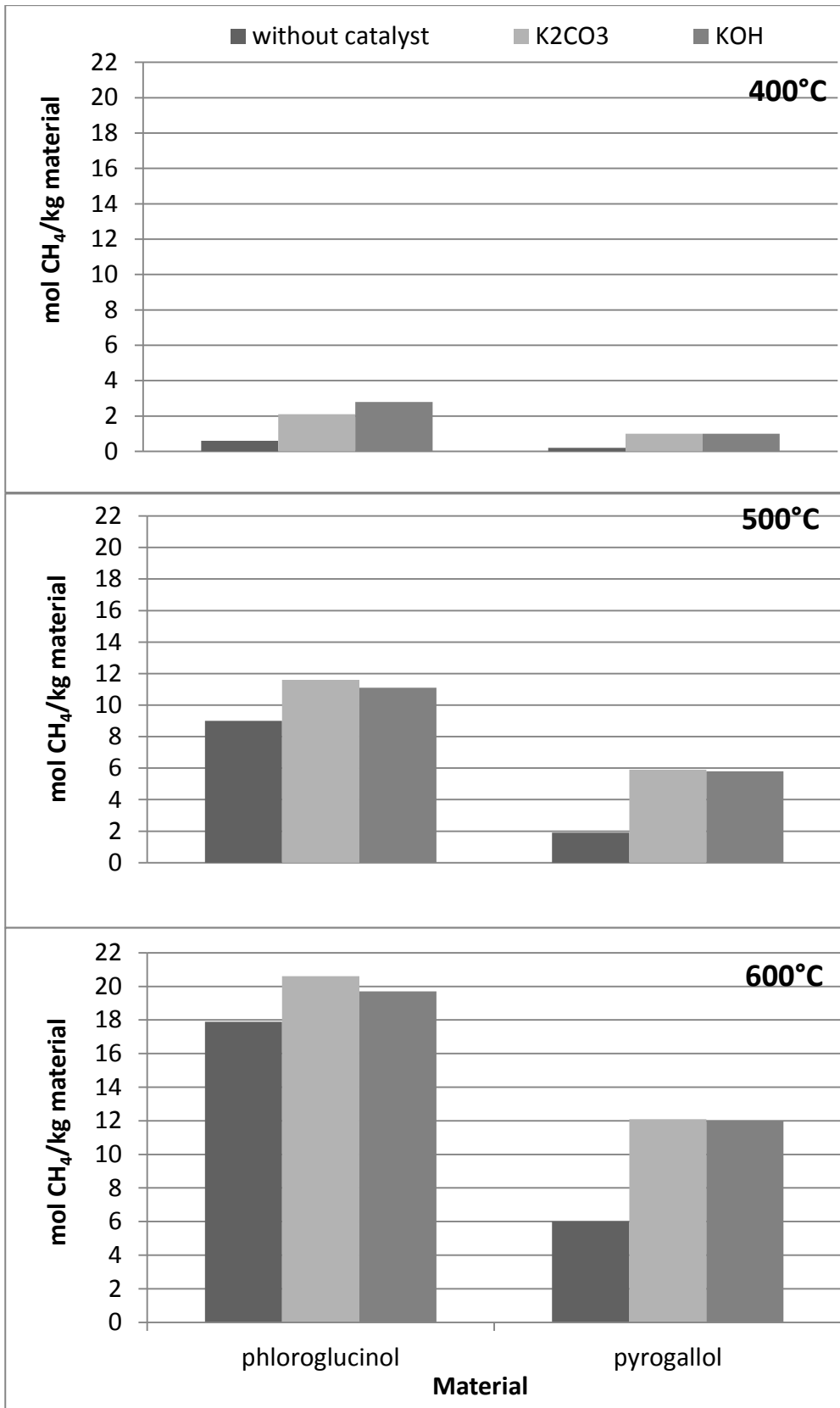


Figure 5.1.11 Temperature and catalyst effects on methane yields of phloroglucinol and pyrogallol. hydrothermal gasification.

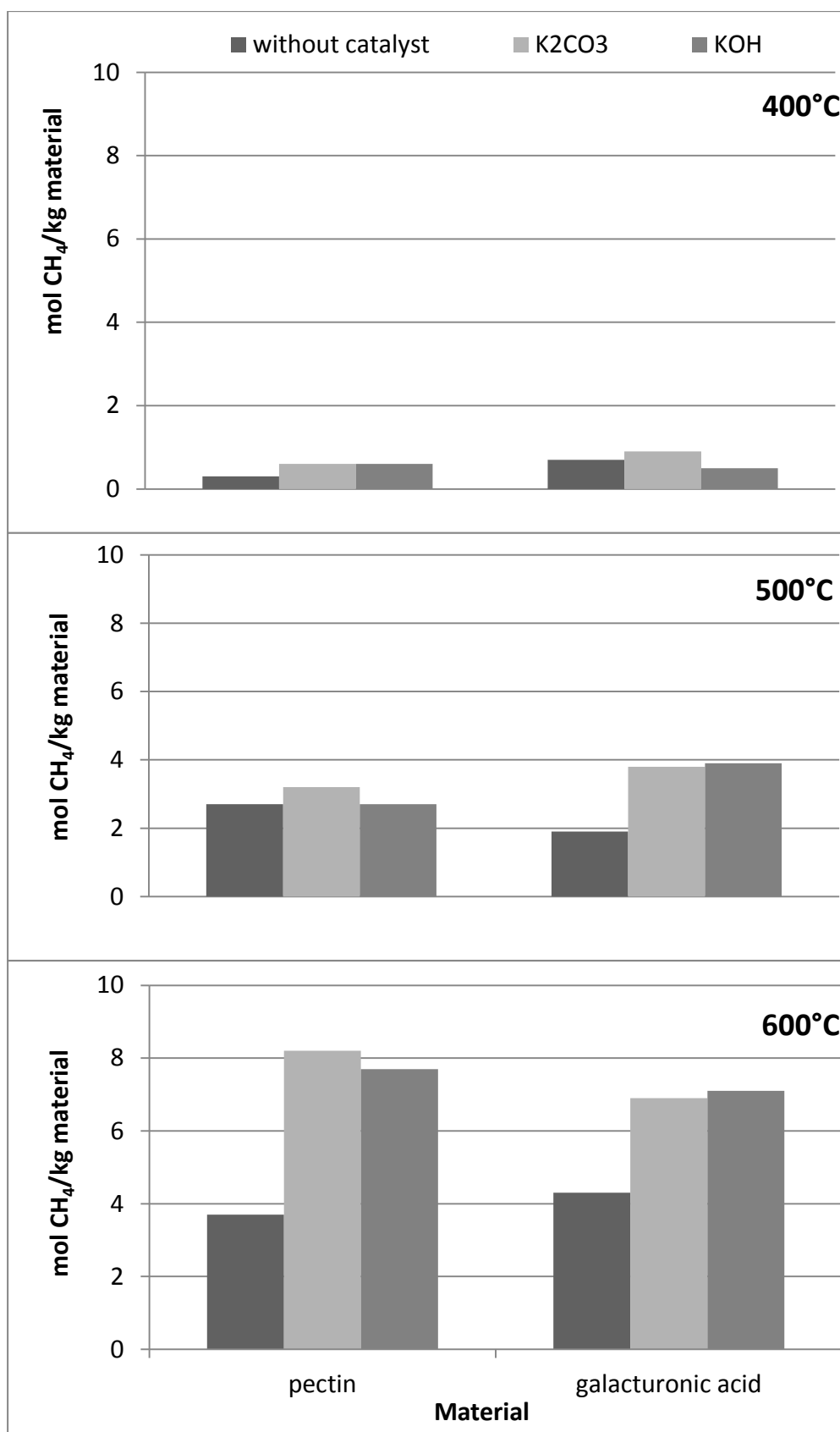


Figure 5.1.12 Temperature and catalyst effects on methane yields of pectin and galacturonic acid hydrothermal gasification.

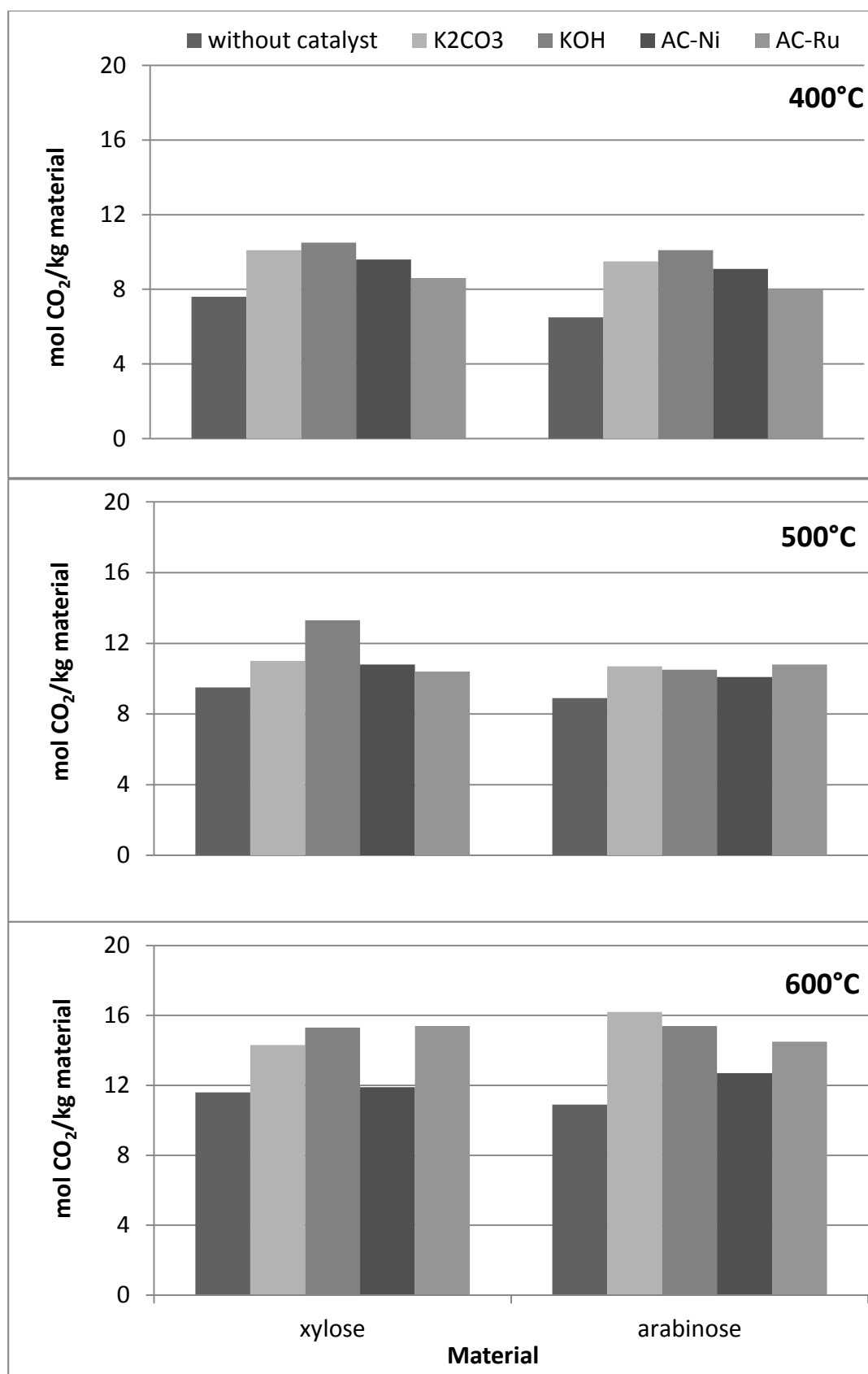


Figure 5.1.13 Temperature and catalyst effects on carbondioxide yields of xylose and arabinose hydrothermal gasification.

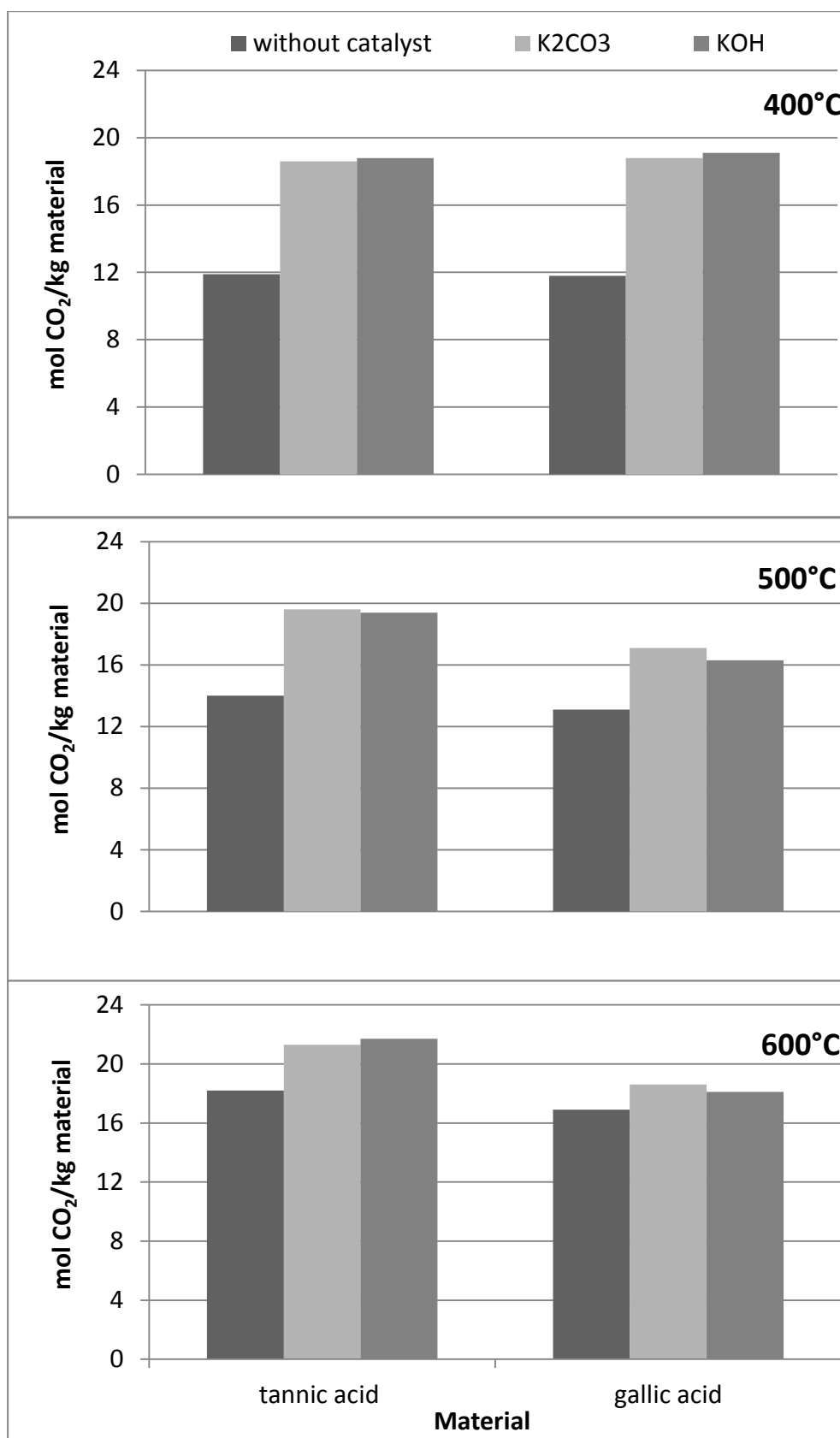


Figure 5.1.14 Temperature and catalyst effects on carbondioxide yields of tannic acid and gallic acid.

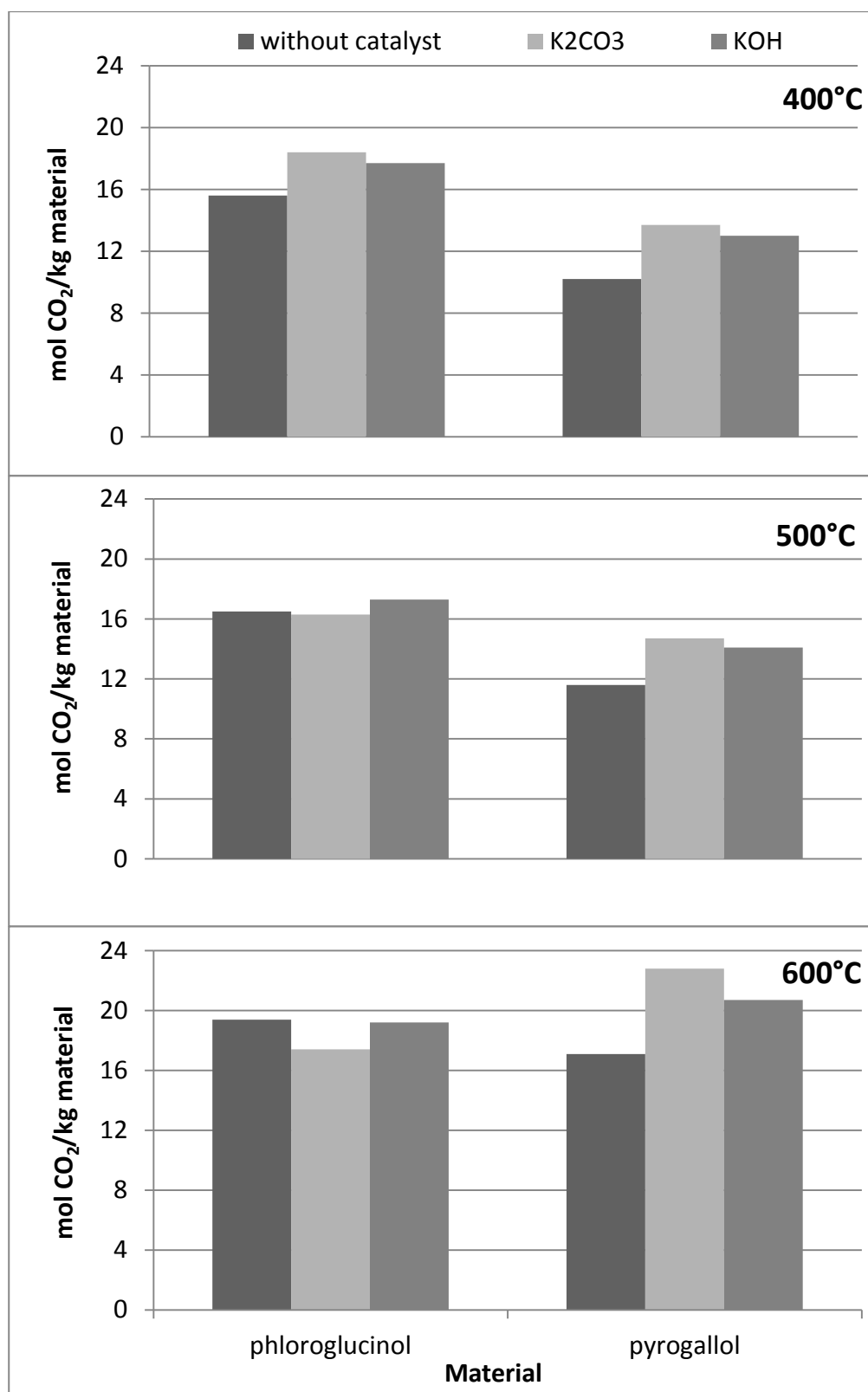


Figure 5.1.15 Temperature and catalyst effects on carbondioxide yields phloroglucinol and pyrogallol.

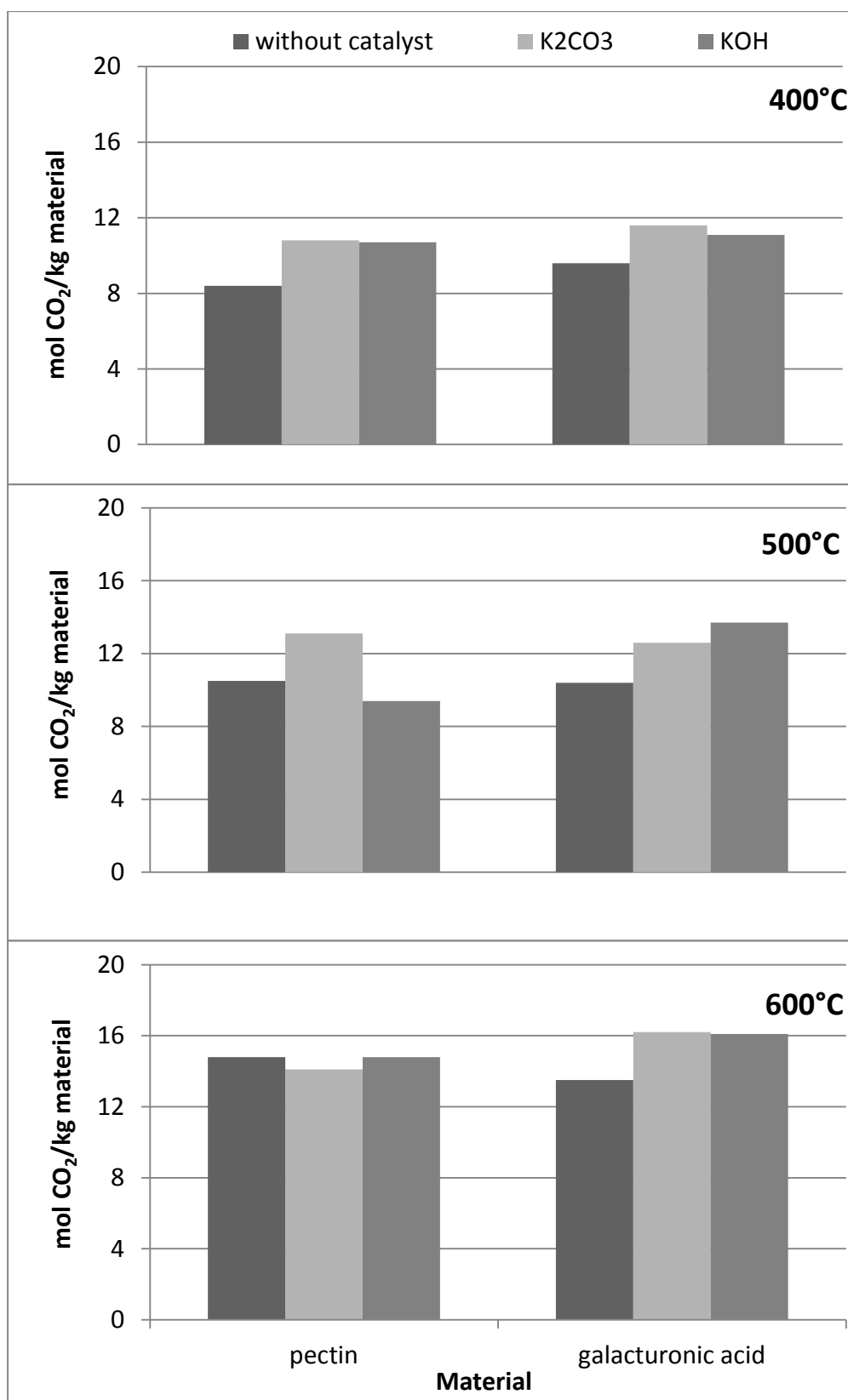


Figure 5.1.16 Temperature and catalyst effects on carbondioxide yields of pectin and galacturonic acid hydrothermal gasification.

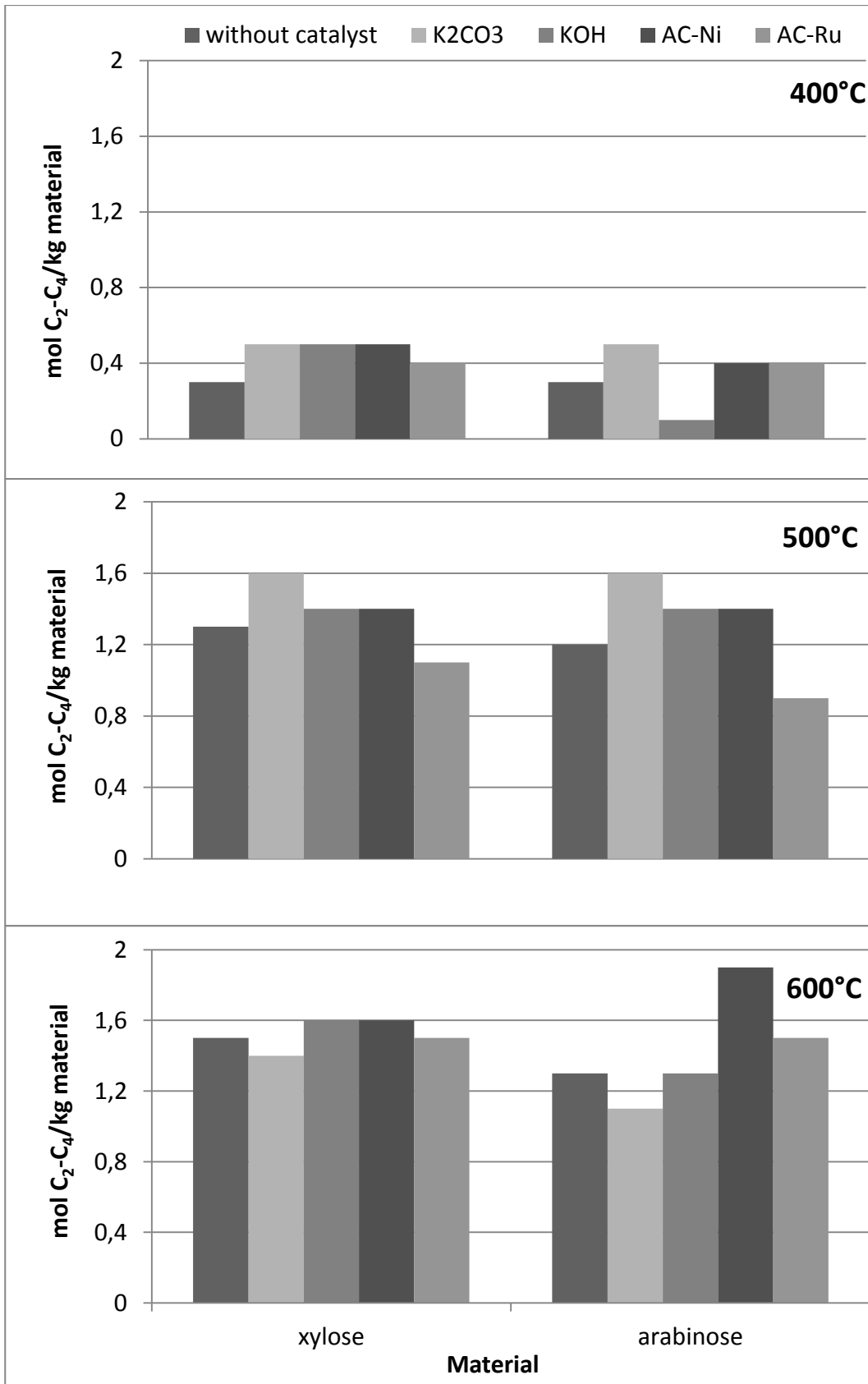


Figure 5.1.17 Temperature and catalyst effects on C₂-C₄ yields of xylose and arabinose hydrothermal gasification.

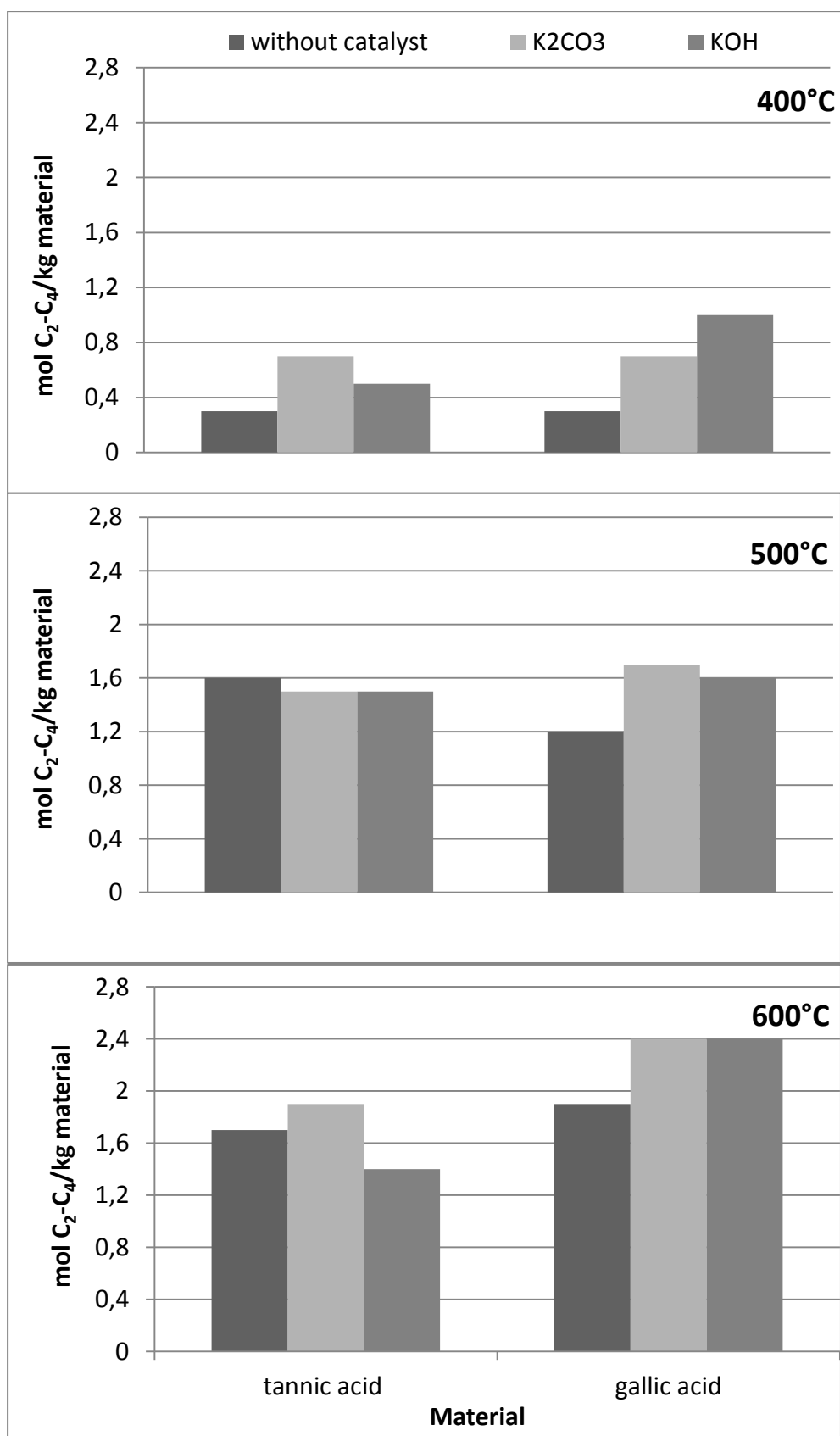


Figure 5.1.18 Temperature and catalyst effects on C_2-C_4 yields of tannic acid and gallic acid.

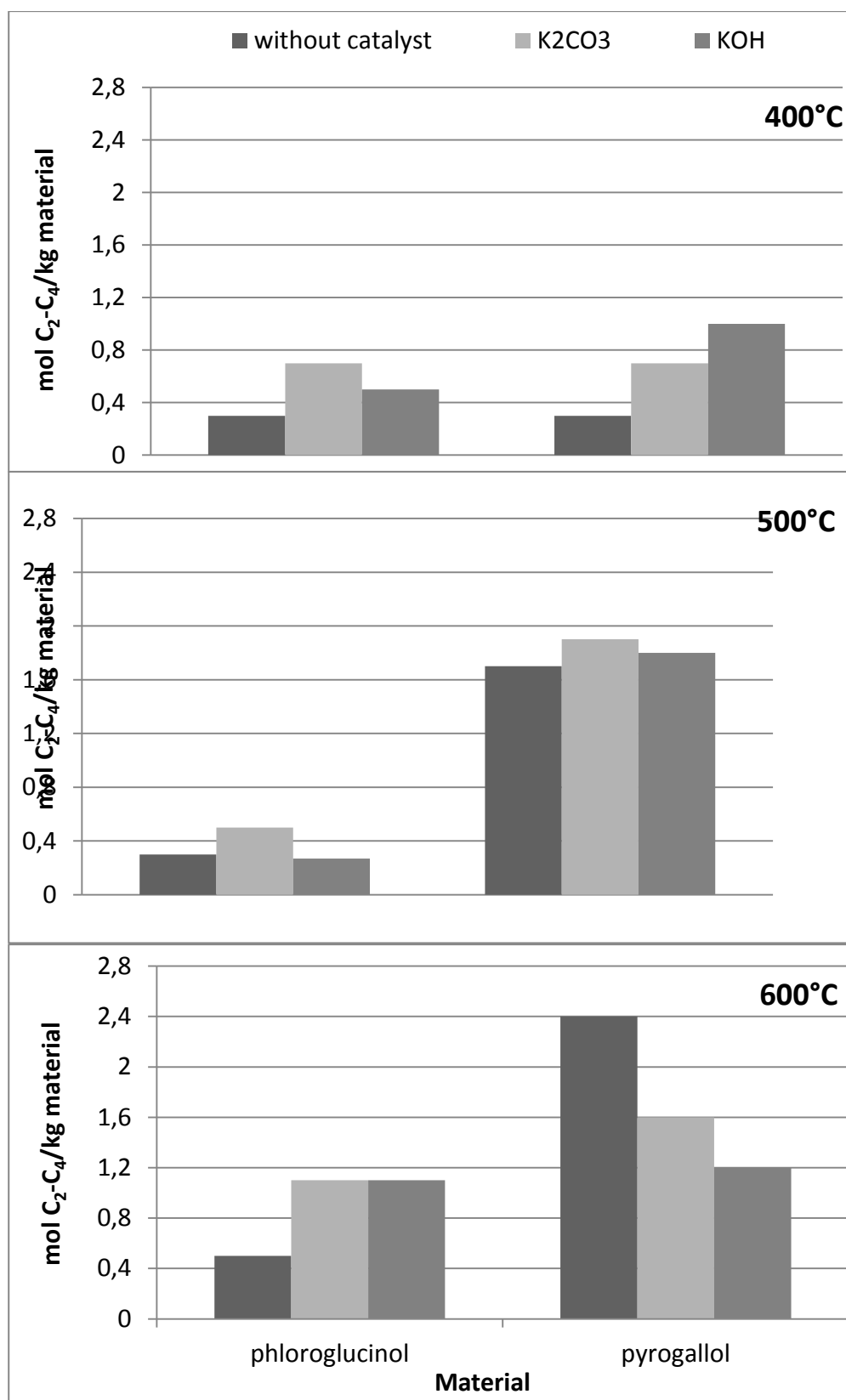


Figure 5.1.19 Temperature and catalyst effects on C_2-C_4 yields of phloroglucinol and pyrogallol.

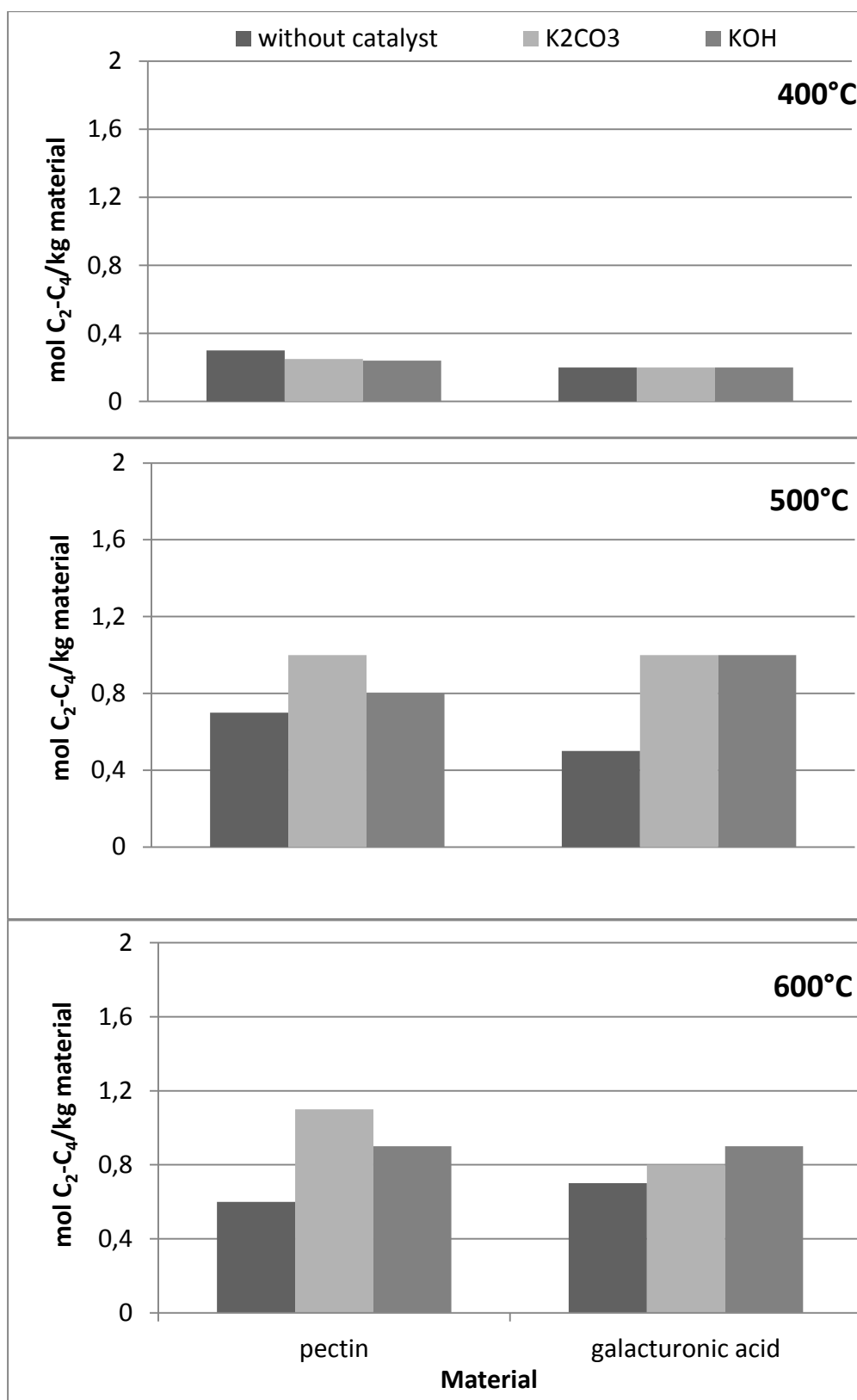


Figure 5.1.20 Temperature and catalyst effects on C_2-C_4 yields of pectin and galacturonic acid hydrothermal gasification.

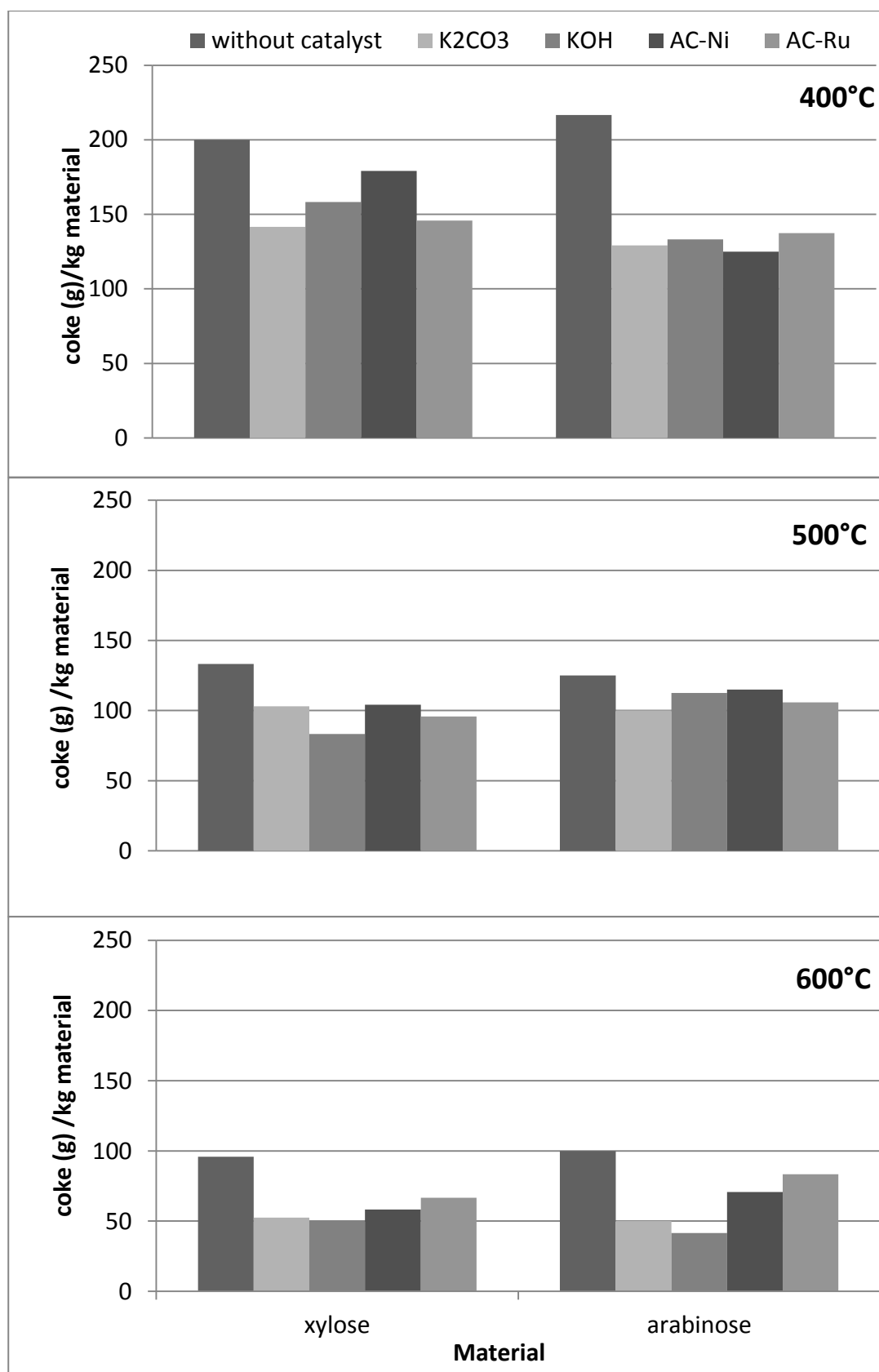


Figure 5.1.21 Temperature and catalyst effects on coke yields of xylose and arabinose hydrothermal gasification.

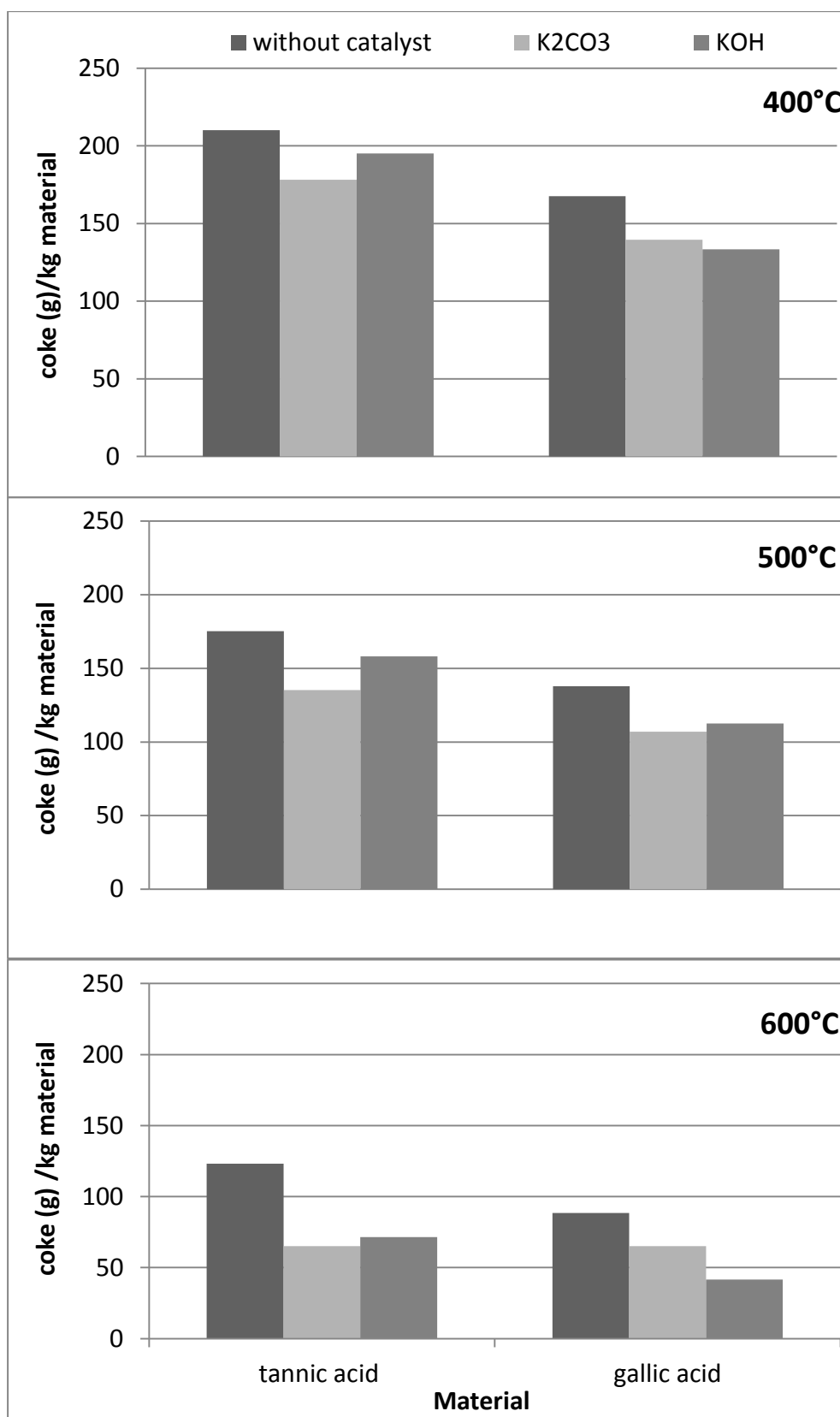


Figure 5.1.22 Temperature and catalyst effects on coke yields of tannic acid and gallic acid.

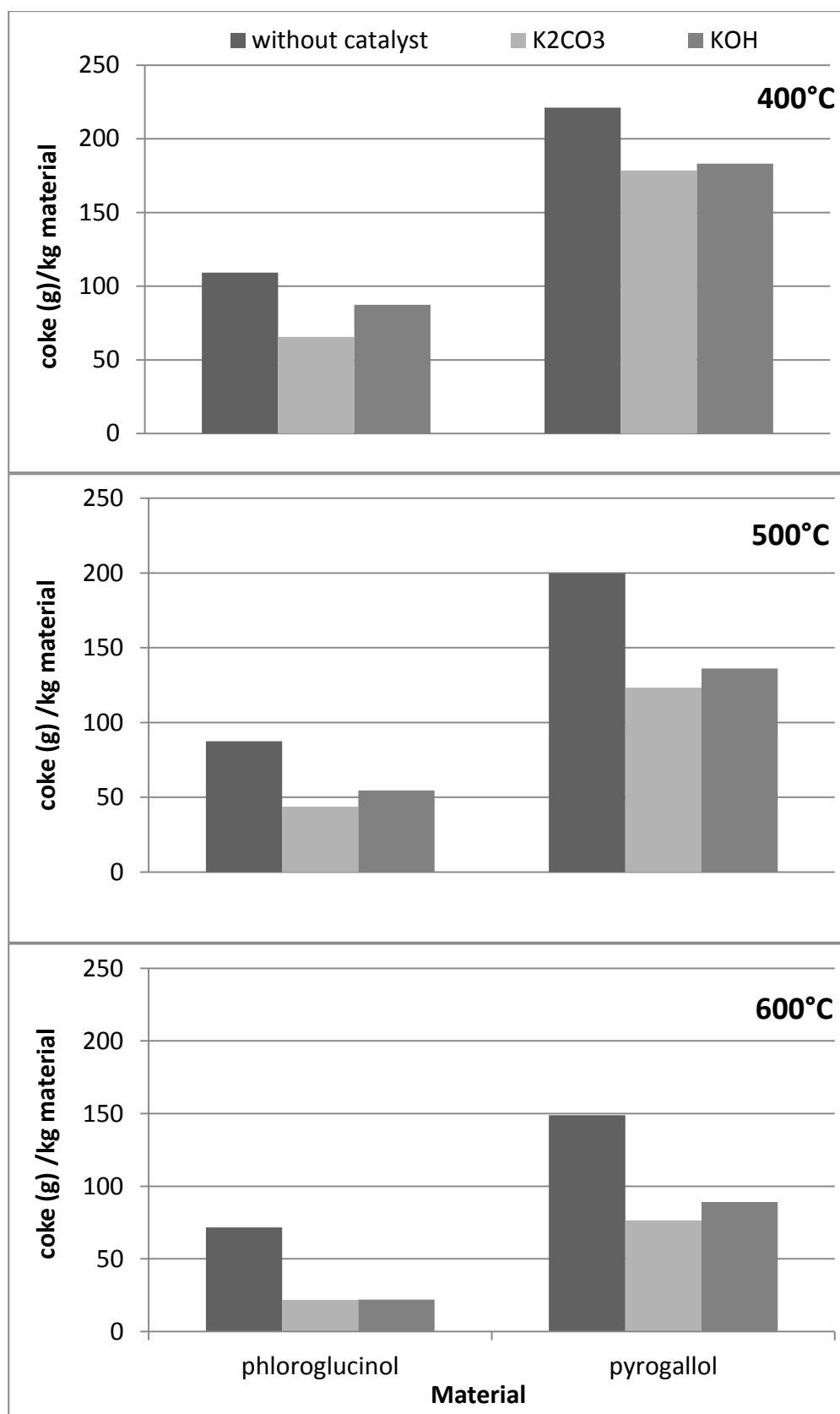


Figure 5.1.23 Temperature and catalyst effects on coke yields of phloroglucinol and pyrogallol.

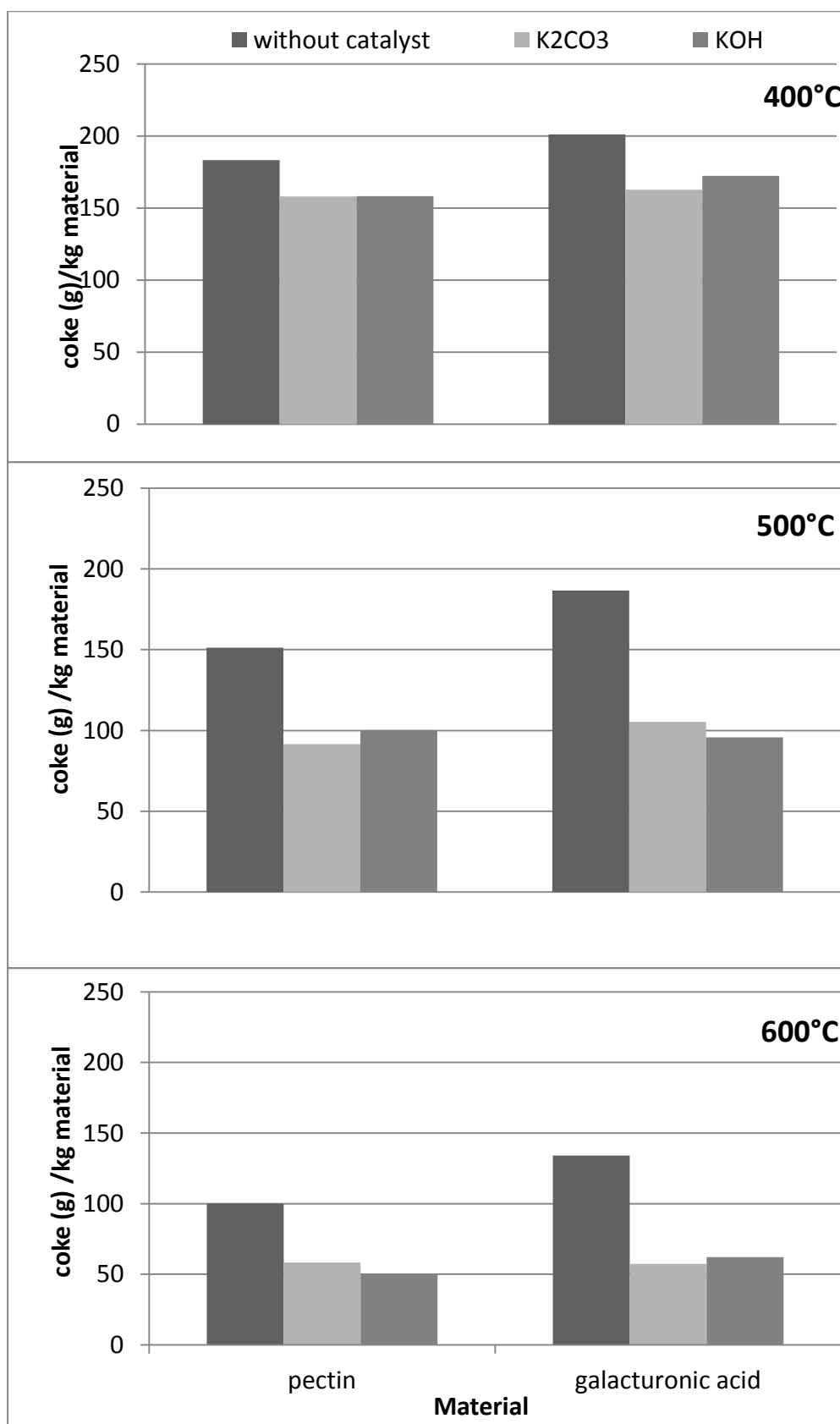


Figure 5.1.24 Temperature and catalyst effects on coke yields of pectin and galacturonic acid hydrothermal gasification.

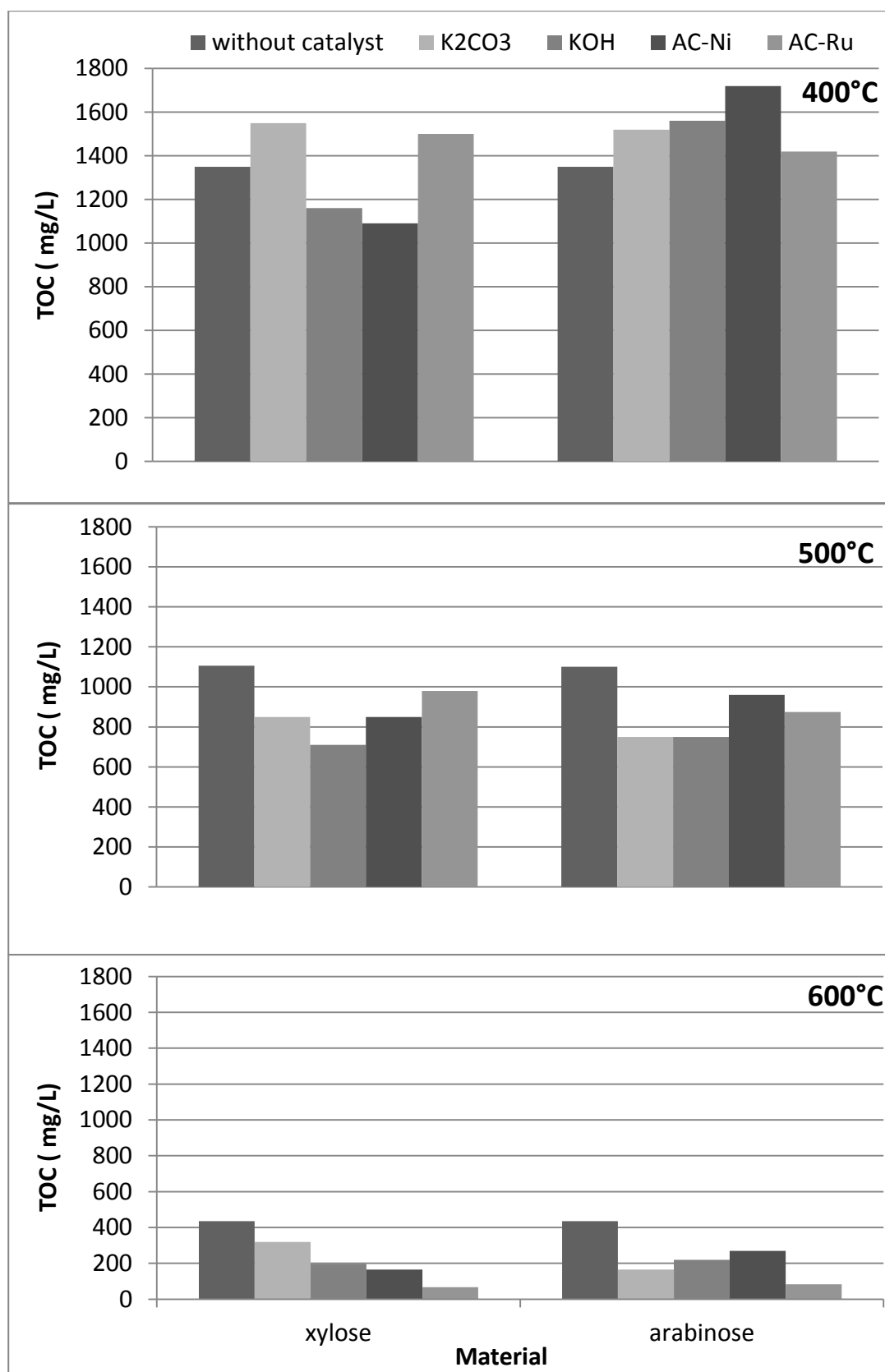


Figure 5.1.25 Temperature and catalyst effects on TOC (mg/L) of xylose and arabinose hydrothermal gasification.

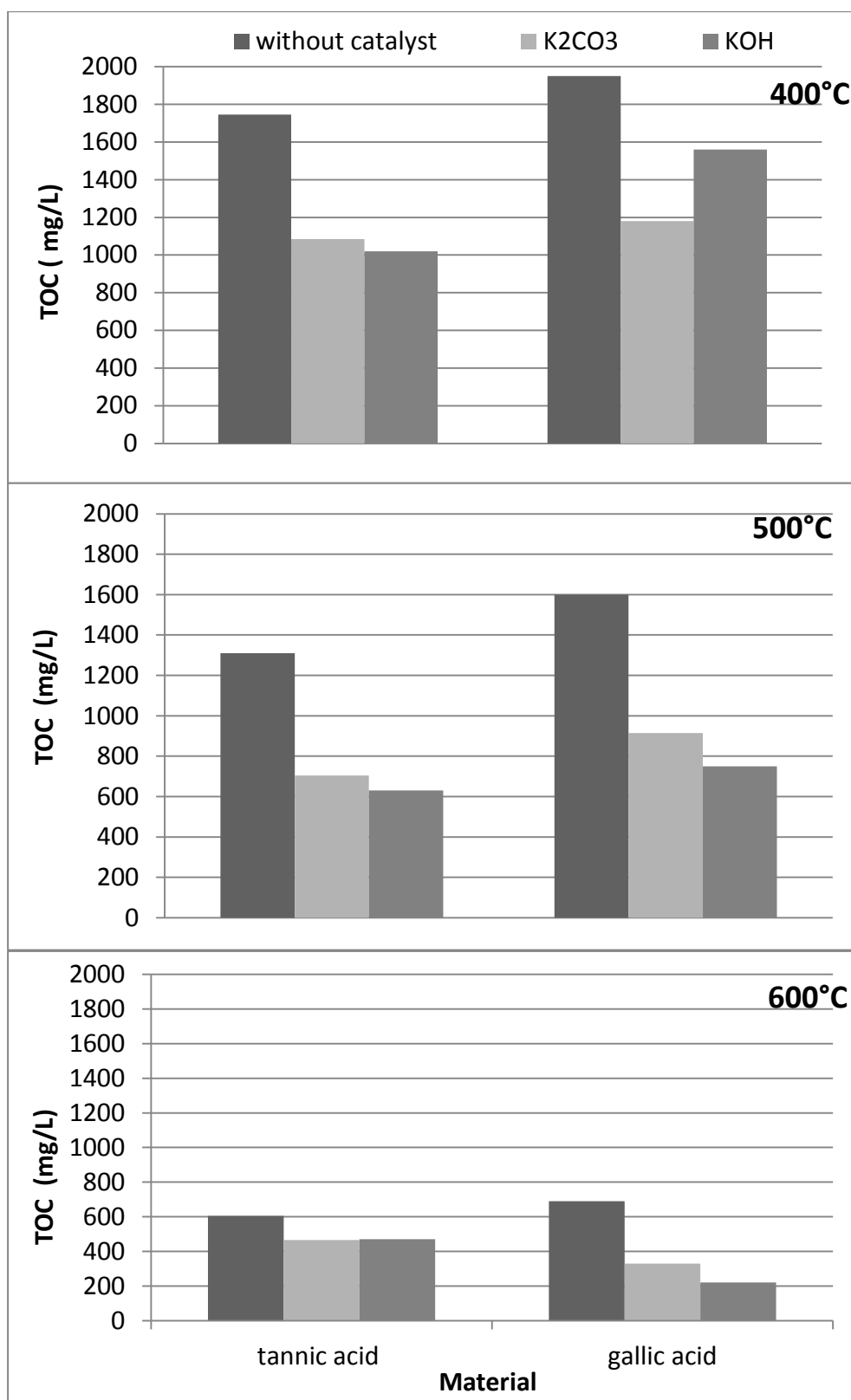


Figure 5.1.26 Temperature and catalyst effects on TOC yields (mg/L) of tannic acid and gallic acid.

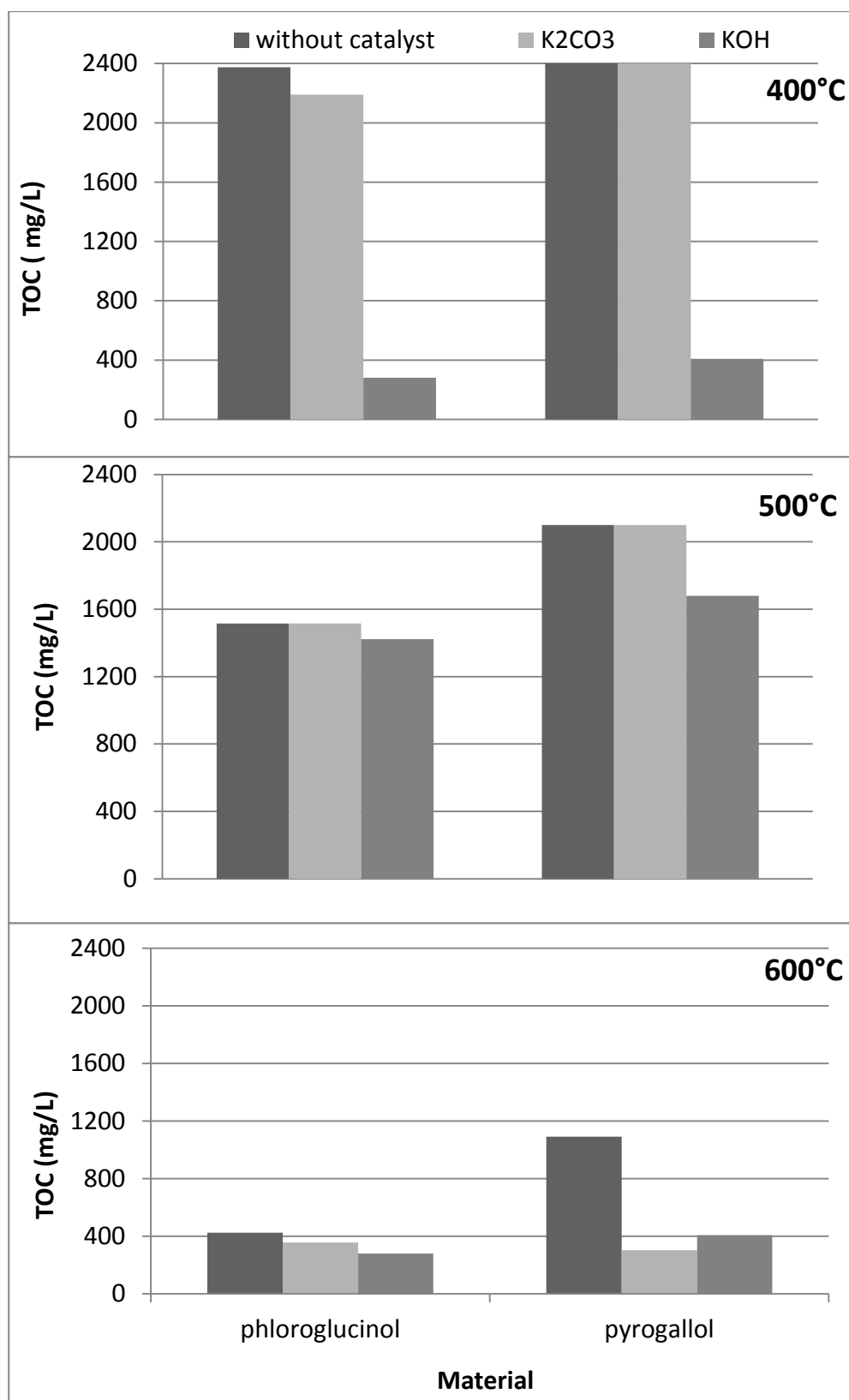


Figure 5.1.27 Temperature and catalyst effects on TOC yields (mg/L) of phloroglucinol and pyrogallol.

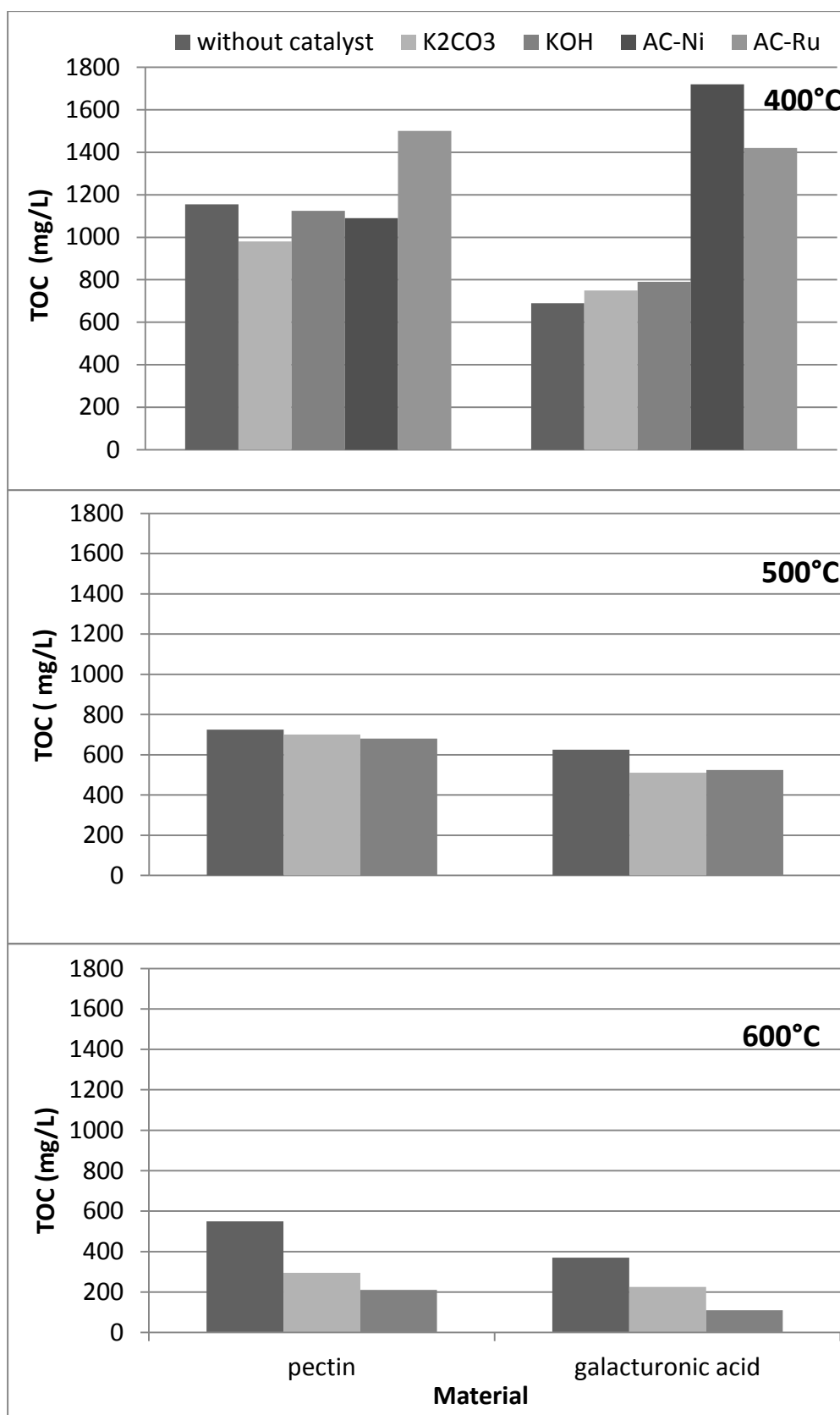


Figure 5.1.28 Temperature and catalyst effects on TOC (mg/L) of pectin and galacturonic acid hydrothermal gasification.

5.2 Influence of Pressure and Catalyst on the Gasification and Gas Composition

In this study, hydrothermal gasification of xylose, arabinose, tannic acid, gallic acid, phloroglucinol, pyrogallol, pectin and galacturonic acid were performed in a batch reactor system at temperature and pressure ranges of 400, 500 and 600°C and 20, 27.5, 35.0 and 42.5 MPa in the absence and presence of K_2CO_3 . The objective of this study was to elucidate the simultaneous effect of the high reaction temperature, high pressure and K_2CO_3 on the gas and liquid product distribution. The influences of temperature, pressure and catalyst were examined in relation to the maximum yields of the H_2 and CH_4 gases and in the reaction pathway of xylose hydrothermal gasification. A total of 0.55-3.5 g of the selected model compound and 10 wt.% K_2CO_3 were well mixed and loaded into the reactor with water. The amount of water was determined by preliminary tests so that desired four pressures (20, 27.5, 35 and 42.5 MPa) for the operating temperatures 400, 500 and 600°C were attained. All experiments were performed in triplicate with a resulting precision of product yields about 5%. Reactor pressure was stabilized at the desired values with precision of $0.5 \pm$ MPa. Tables 20-43 display the experimental conditions and experimental results obtained in the absence and in the presence of K_2CO_3 with increasing pressure and constant temperatures 400, 500 and 600°C. The product distribution and products composition are strongly affected by the reaction temperature, pressure and catalyst. The effect of temperature is significant in the reaction temperature range 400-600°C gasification efficiency is increased sharply with temperature while liquefaction, residue amount and TOC in liquid product reduced with it. Pressure effect on gas yields, on hydrogen yields and methane yields of xylose, arabinose, tannic acid, gallic acid, phloroglucinol, pyrogallol, pectin and galacturonic acid hydrothermal gasification in the presence and absence of K_2CO_3 were given in the Figures 5.2.1-5.1.21, respectively. By addition of K_2CO_3 gasification was increased and the formation of residue decreased. With increasing pressure, gasification decreased and liquefaction slightly increased. The highest gas product and the lowest residue amount were obtained at the highest temperature of 600°C and at the lowest pressure of 20 MPa in the presence of K_2CO_3 . The highest liquid product was found at the lowest temperature of 400°C and at the highest pressure

in the presence of K_2CO_3 . The properties of water such as dielectric constant, density and ion product are changing differently by temperature and pressure effects. The dielectric constant decreases by increasing the temperature while it slightly increases by increasing the pressure. The solubility of organics and gases could be influenced through variations in the dielectric constant. The water density decreases with the temperature at constant pressure and increases with the pressure. The water density can be changed from liquid to gas phase by varying the temperature and pressure. The pressure has no significant effect on the ion product of water at the temperatures lower than $400^\circ C$. However, at the high temperatures, water loses its ionic property with decreasing pressure and ion reaction rate increases with increasing pressure. Supercritical water gasification studies with the xylose, arabinose, tannic acid, gallic acid, phloroglucinol, pyrogallol, pectin and galacturonic acid showed that CO_2 is the main product under these experimental conditions. CO_2 yield was found to be maximum value at the highest reaction temperature and the lowest reaction pressure with catalyst addition (Tables 20-43). The highest second product hydrogen yield in the gas phase has a tendency to increase with increasing temperature, addition of K_2CO_3 and decreasing pressure. H_2 and CO_2 yields decrease with increasing pressure at constant temperature while methane yield increases, since hydrogen and carbon dioxide react at low temperatures to form alkanes and water (Cortright et al., 2002). Gases such as hydrogen are mainly formed via free-radical reactions, which means that the yield of gases increases drastically above the critical temperature and decreases with pressure (Kruse et., 2003). Also the reaction of hydrogen with carbon dioxide to produce methane through the methanation reactions (Eqns.16 and 17) would reduce the production of hydrogen gas. As seen from the Tables 20-43, very low yields of carbonmonoxide was obtained for all experimental conditions. Carbonmonoxide was consumed through the water-gas shift reaction (Eqn. 6) and methanation reaction (Eqns.16 and 17).

Methane yield increased with increasing temperature and pressure by methanation reactions (Eqns 16 and 17) and methane formation (Eqn. 10). According to the Le Chatelier principle, methane formation is preferred at higher pressures.

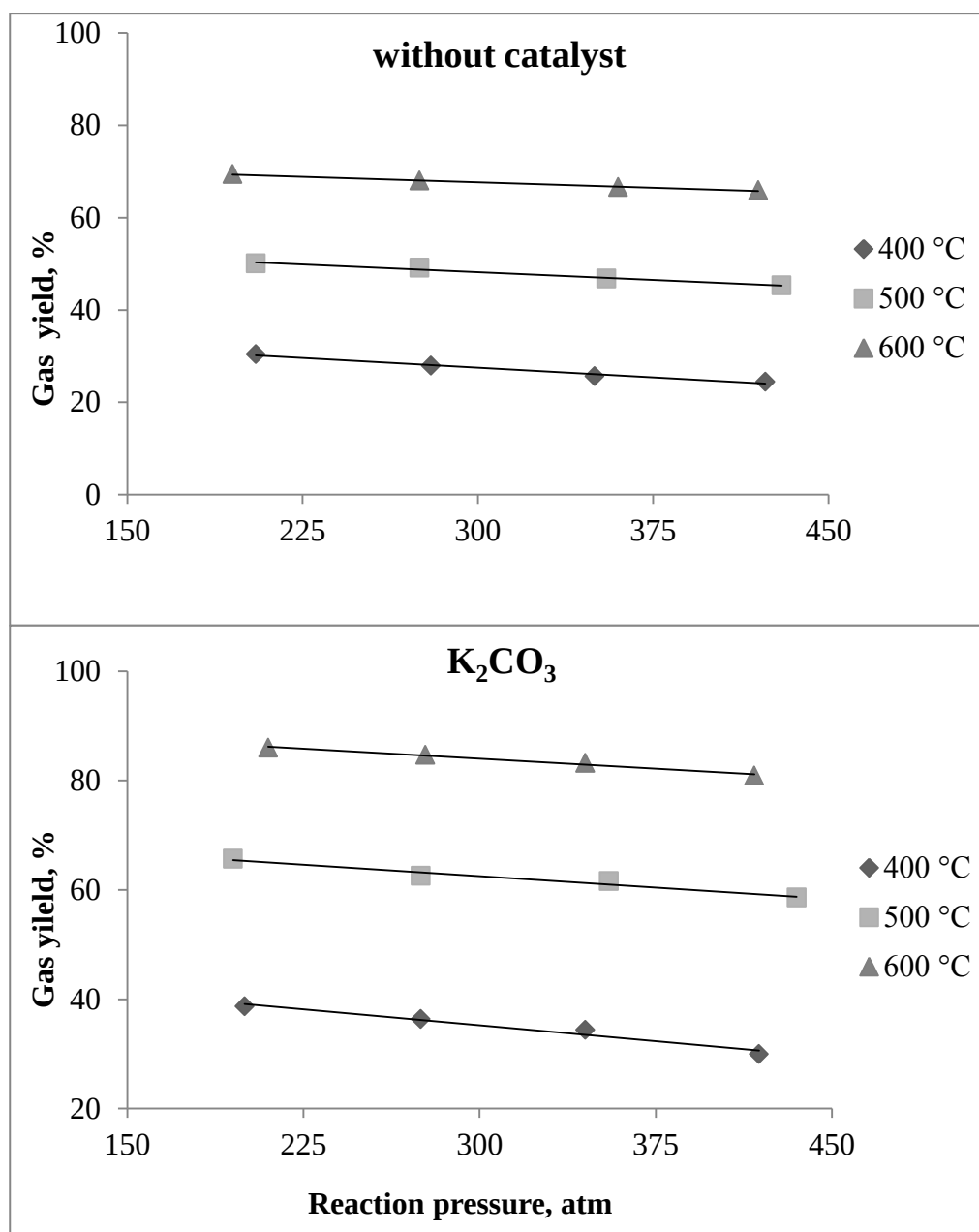


Figure 5.2.1 Pressure effect on gas yield of xylose hydrothermal gasification in the presence and absence of K₂CO₃.

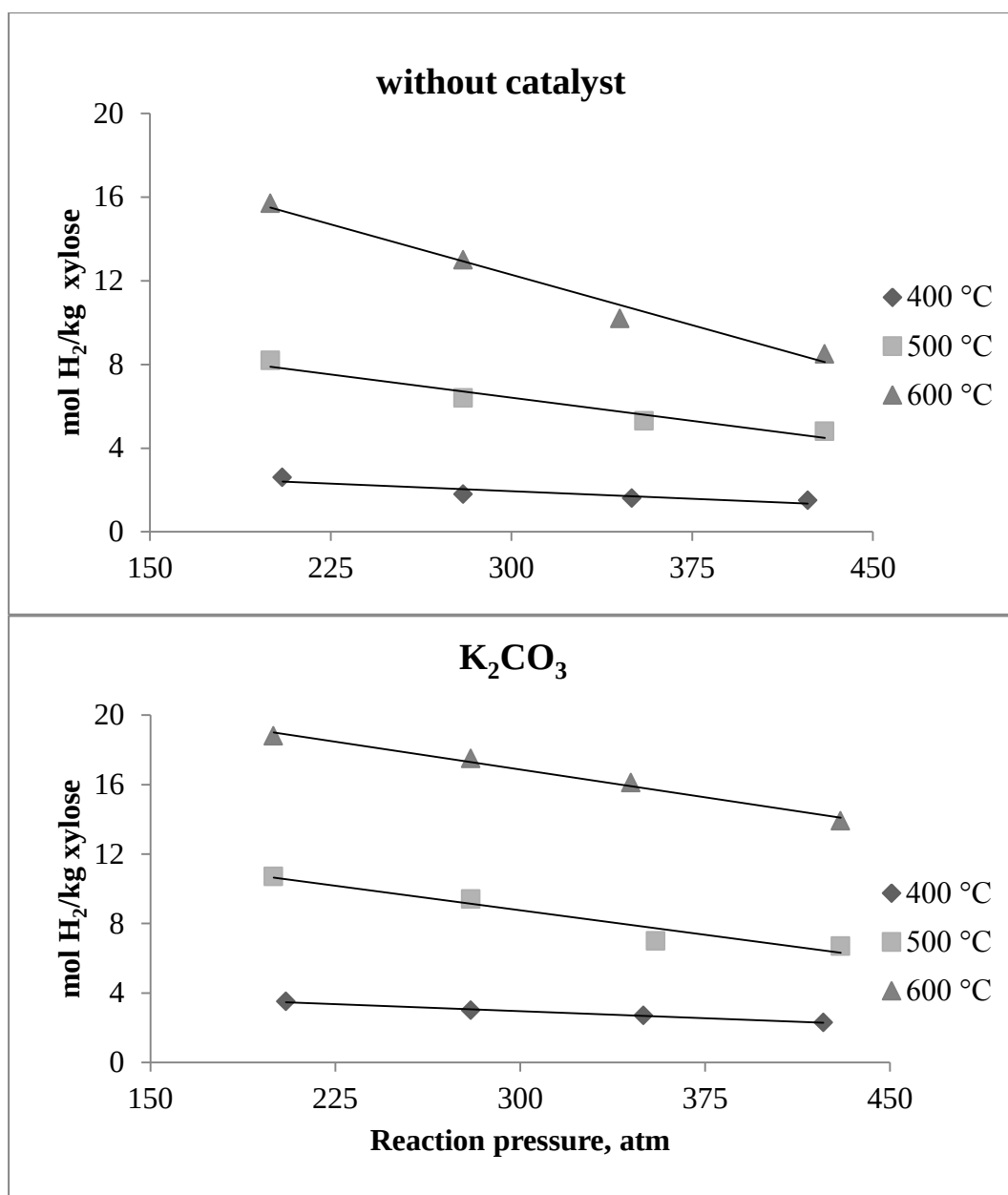


Figure 5.2.2 Pressure effect on hydrogen yield of xylose hydrothermal gasification in the presence and absence of K₂CO₃.

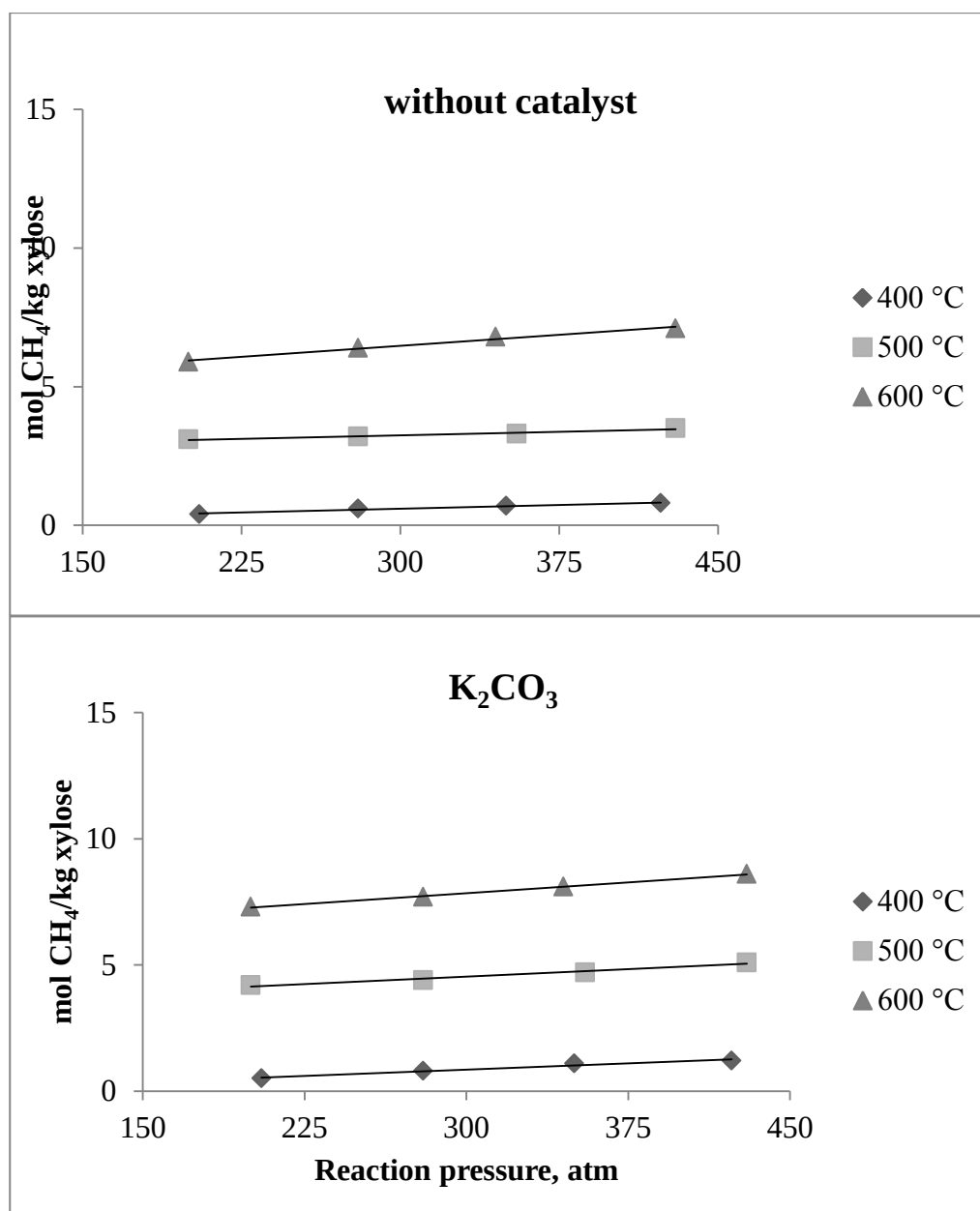


Figure 5.2.3 Pressure effect on methane yield of xylose hydrothermal gasification in the presence and absence of K₂CO₃.

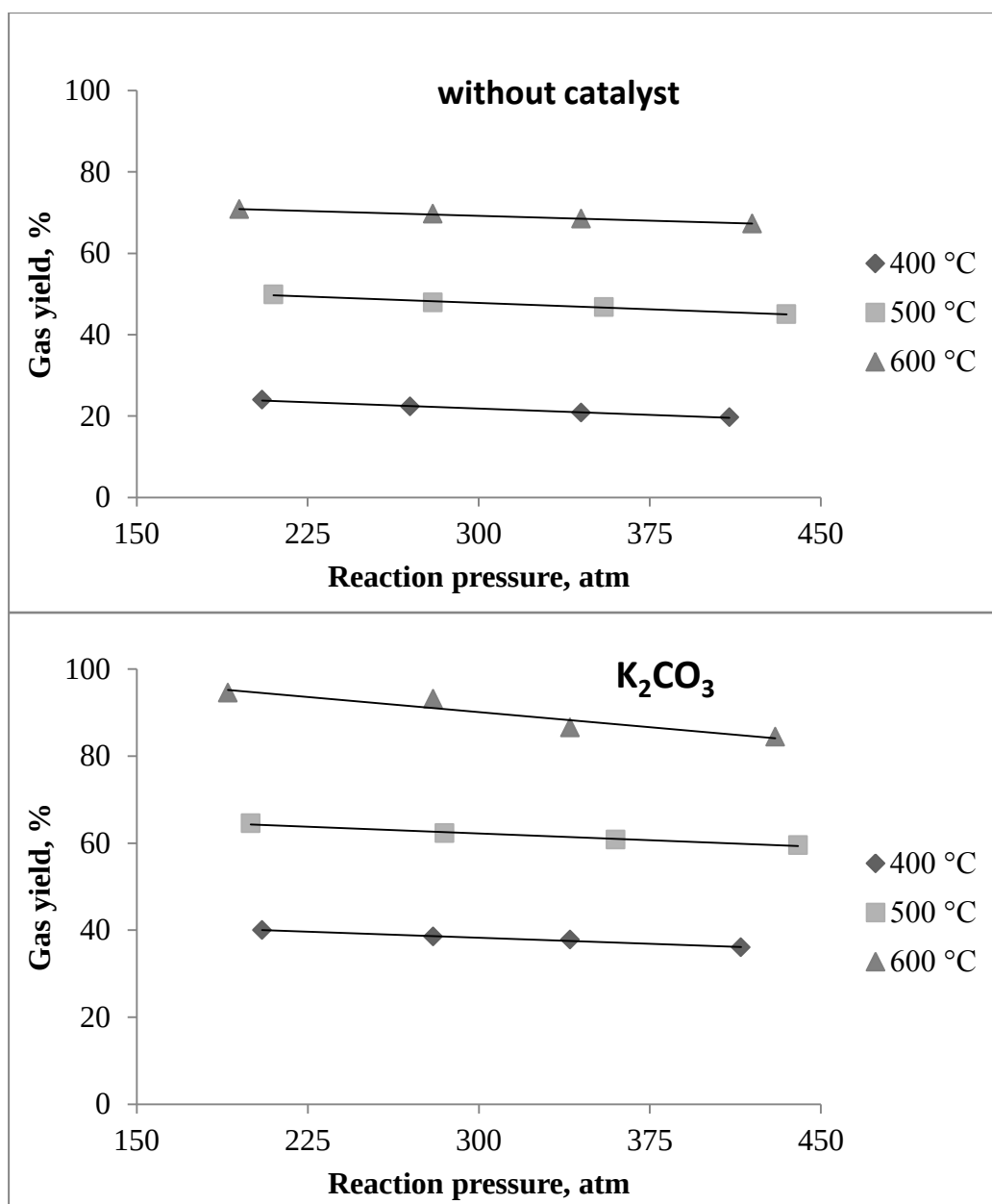


Figure 5.2.4 Pressure effect on gas yield of arabinose hydrothermal gasification in the presence and absence of K₂CO₃.

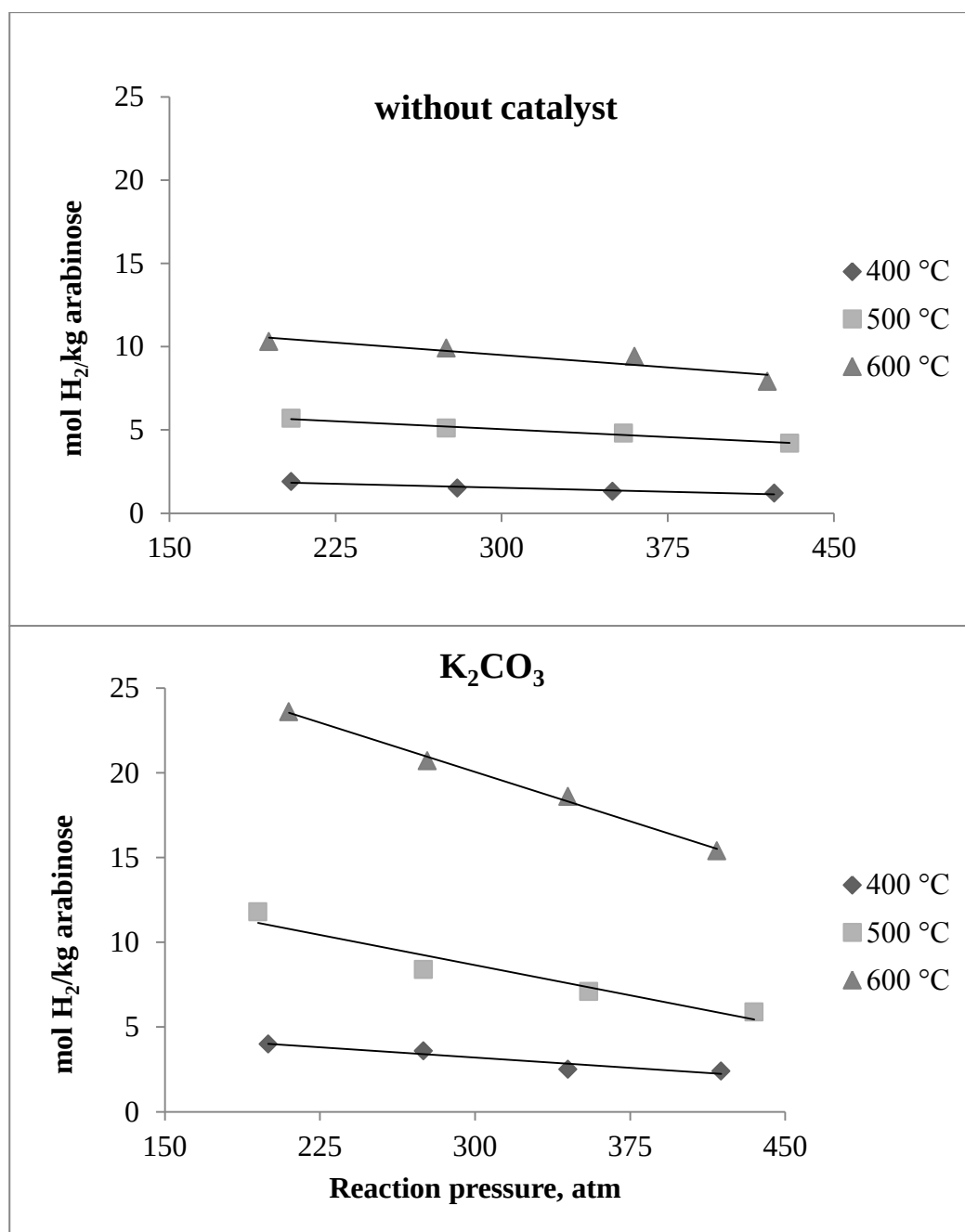


Figure 5.2.5 Pressure effect on hydrogen yield of arabinose hydrothermal gasification in the presence and absence of K₂CO₃.

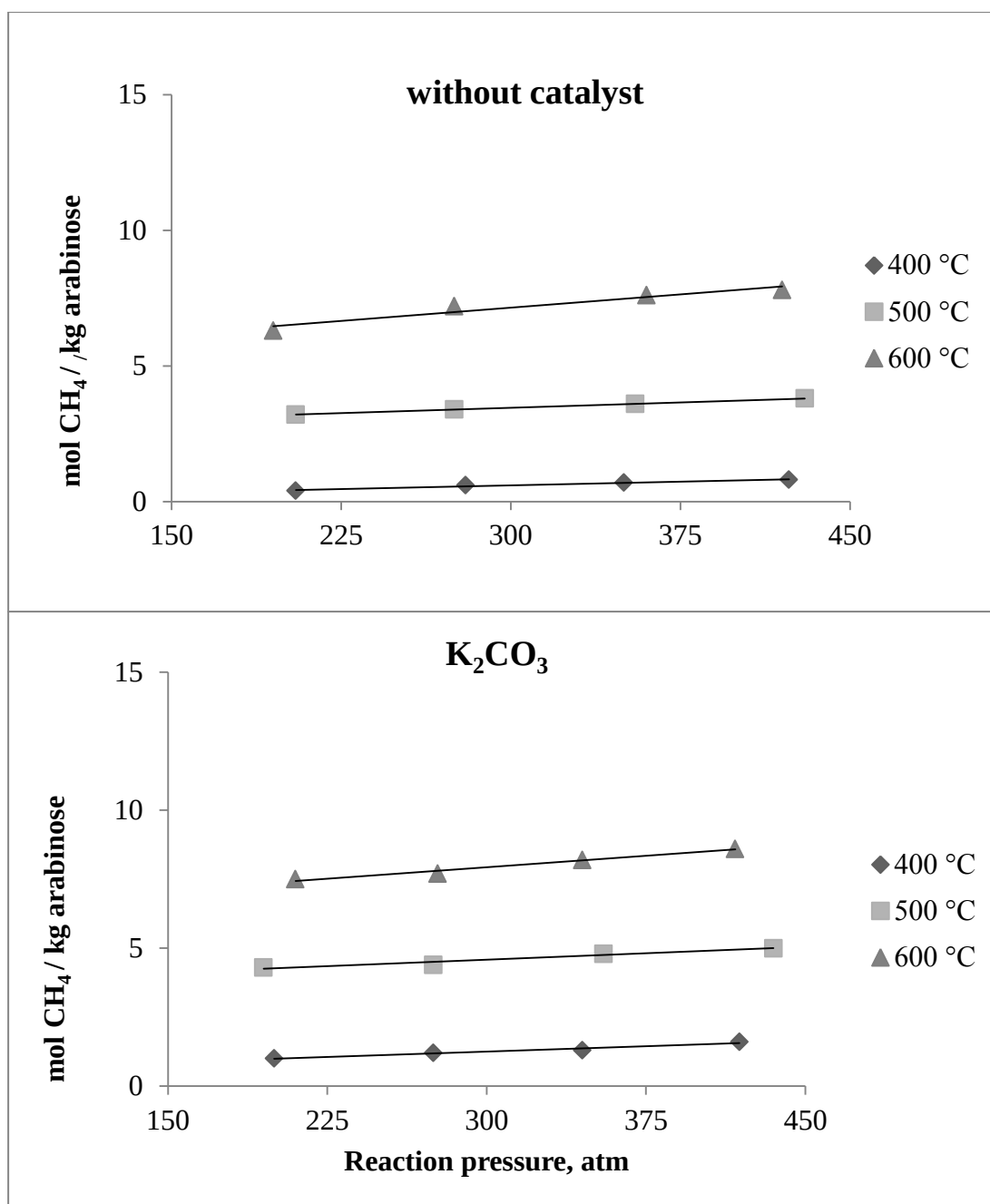


Figure 5.2.6 Pressure effect on methane yield of arabinose hydrothermal gasification in the presence and absence of K₂CO₃.

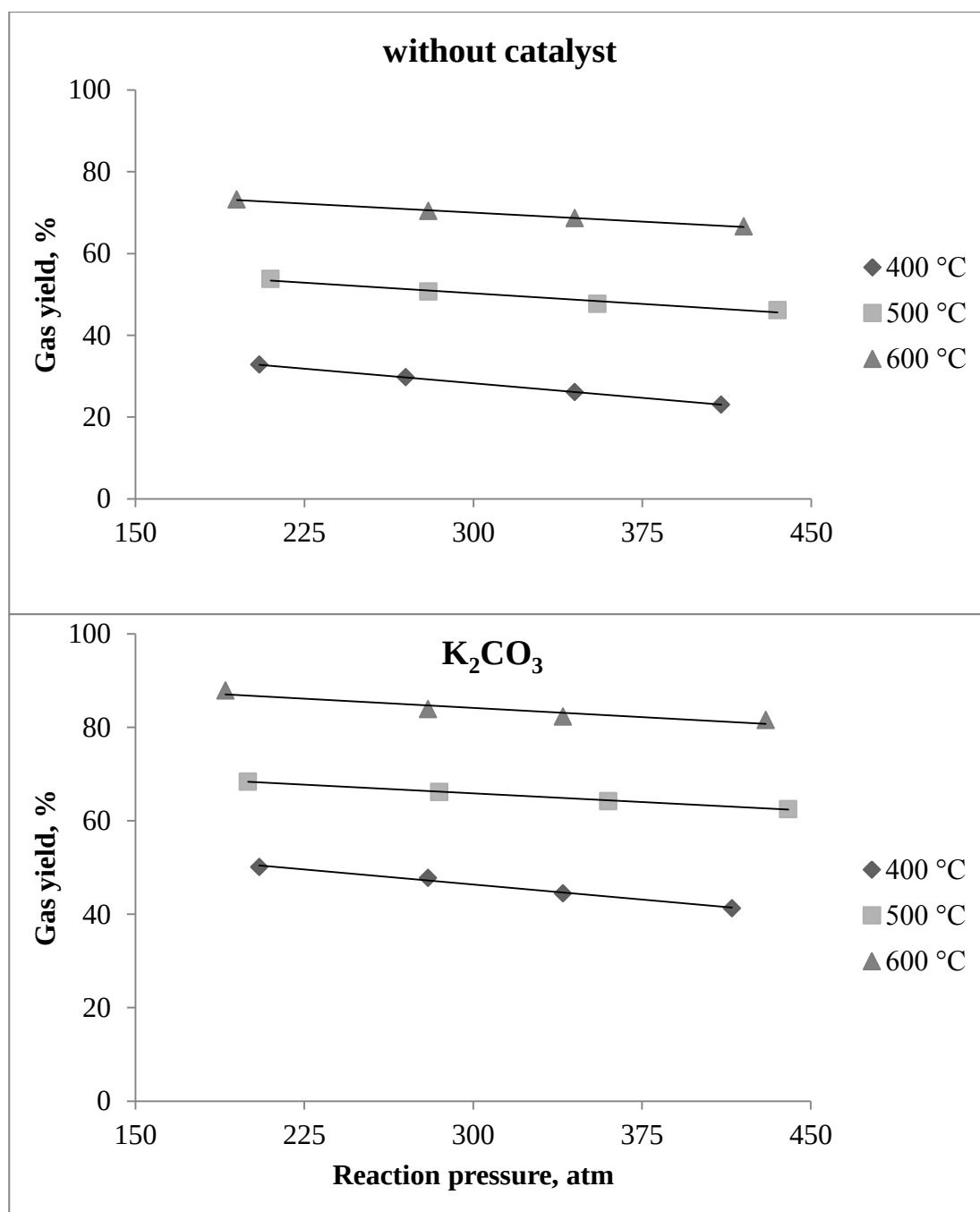


Figure 5.2.7 Pressure effect on gas yield of tannic acid hydrothermal gasification in the presence and absence of K₂CO₃.

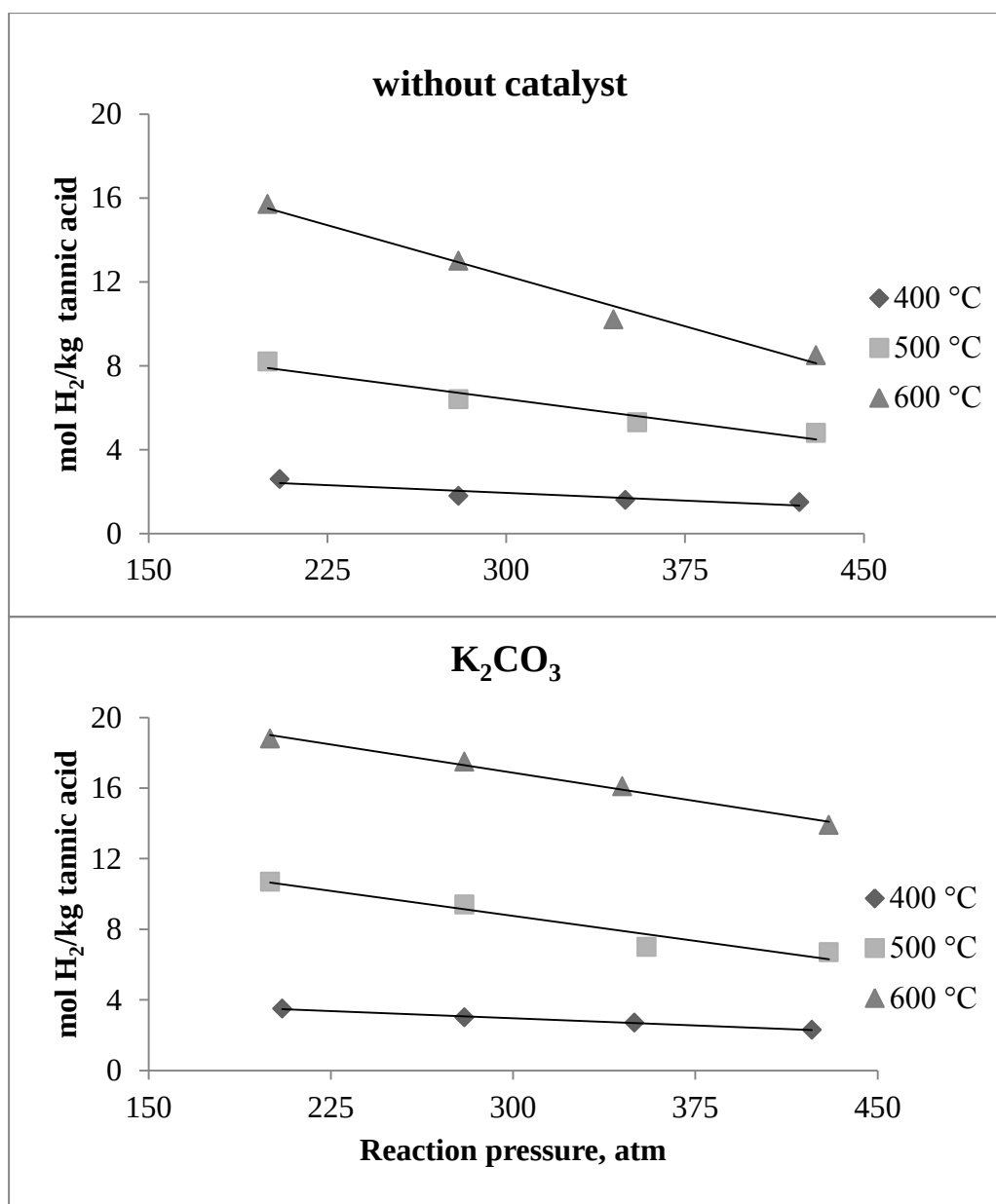


Figure 5.2.8 Pressure effect on hydrogen yield of tannic acid hydrothermal gasification in the presence and absence of K₂CO₃.

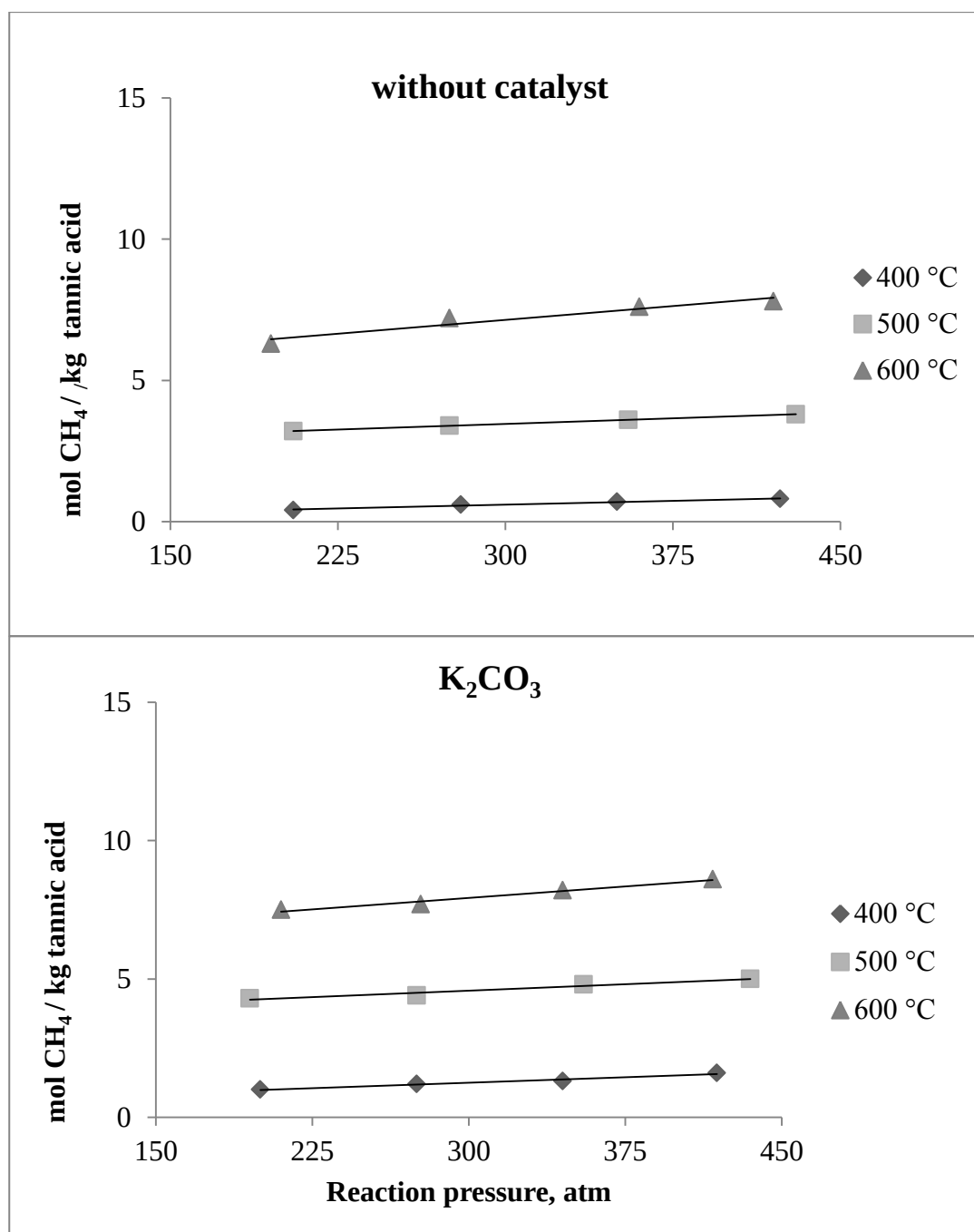


Figure 5.2.9 Pressure effect on methane yield of tannic acid hydrothermal gasification in the presence and absence of K₂CO₃.

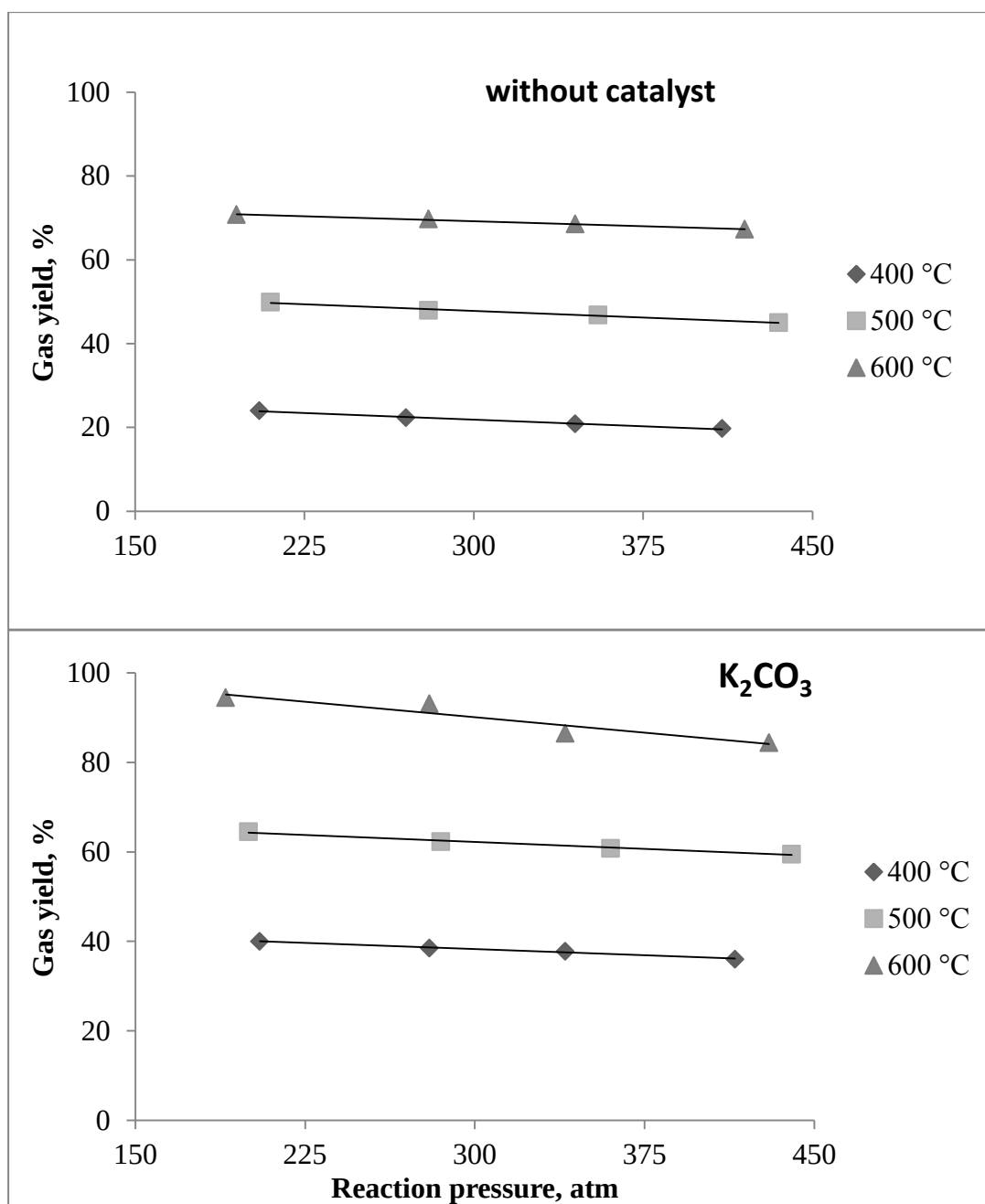


Figure 5.2.10 Pressure effect on gas yield of gallic acid hydrothermal gasification in the presence and absence of K₂CO₃.

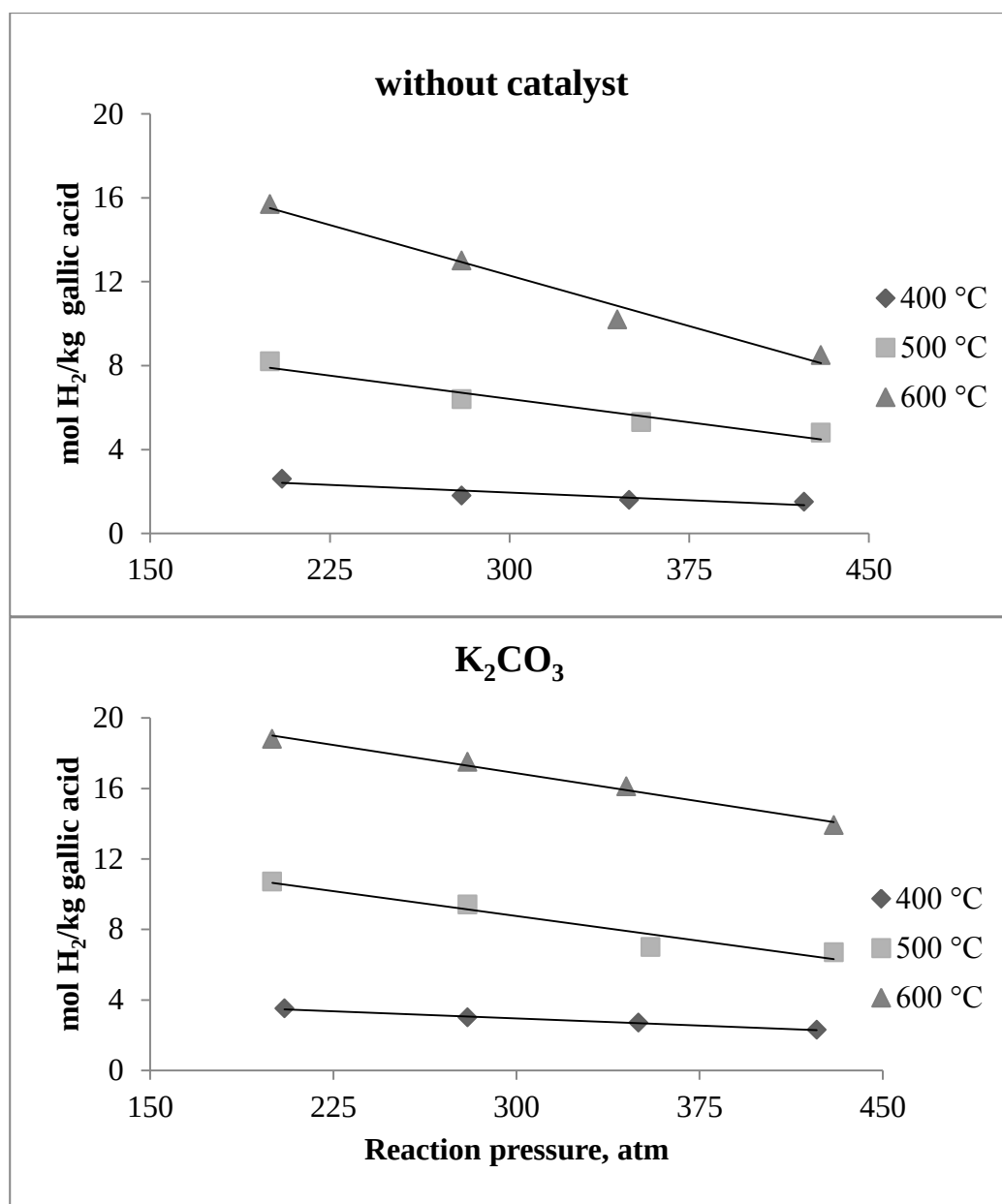


Figure 5.2.11 Pressure effect on hydrogen yield of gallic acid hydrothermal gasification in the presence and absence of K_2CO_3 .

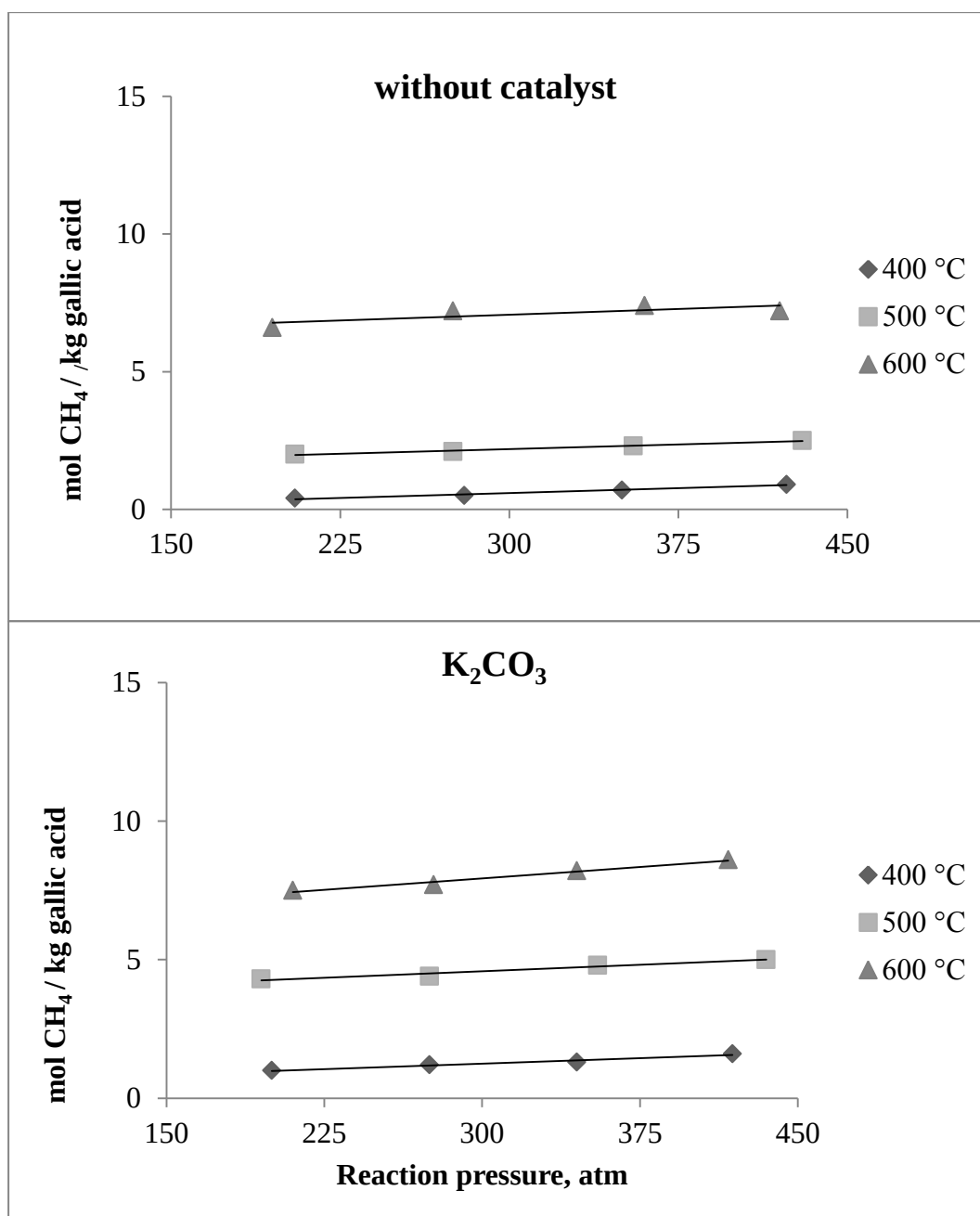


Figure 5.2.12 Pressure effect on methane yield of gallic acid hydrothermal gasification in the presence and absence of K₂CO₃.

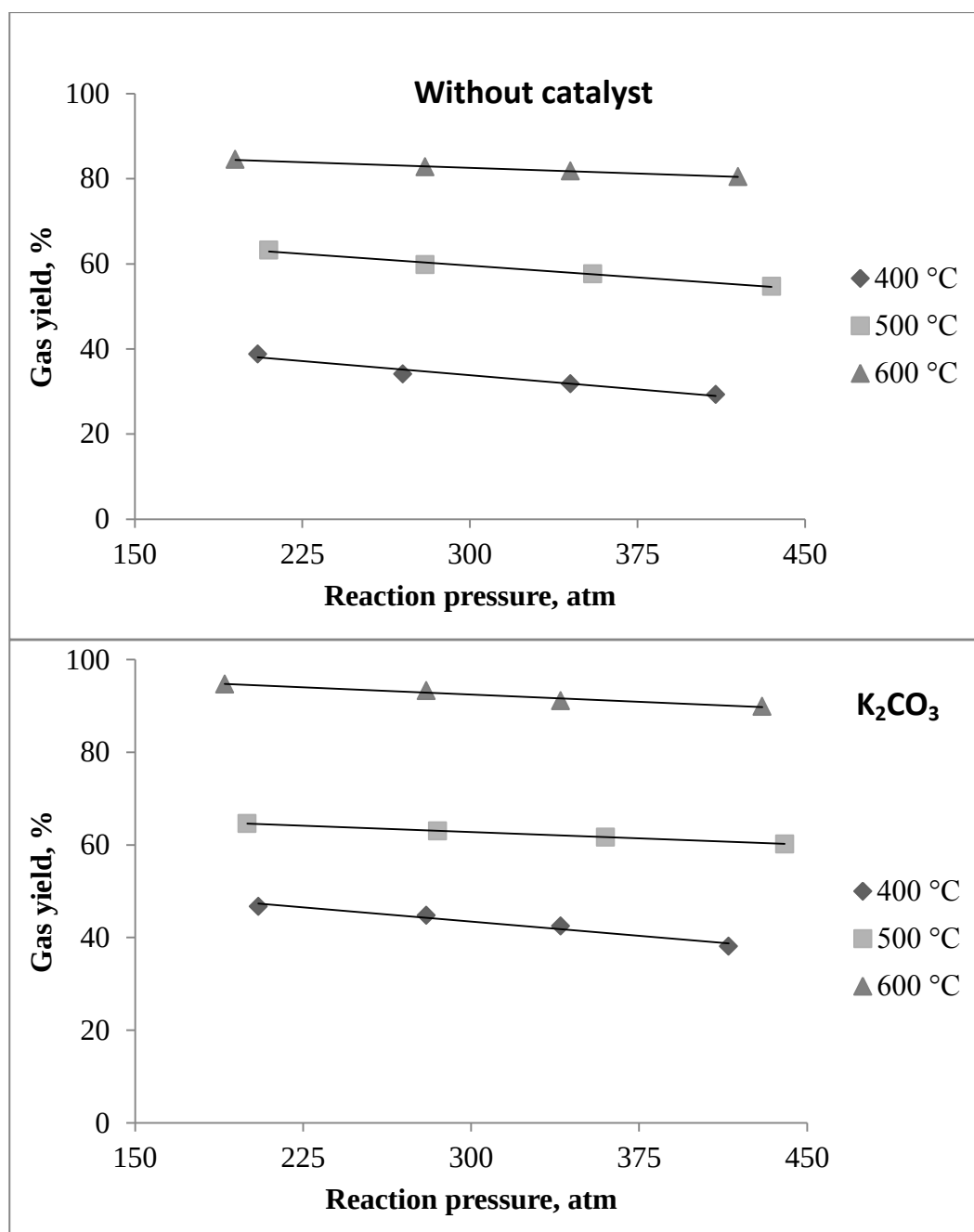


Figure 5.2.13 Pressure effect on gas yield of phloroglucinol hydrothermal gasification in the presence and absence of K₂CO₃.

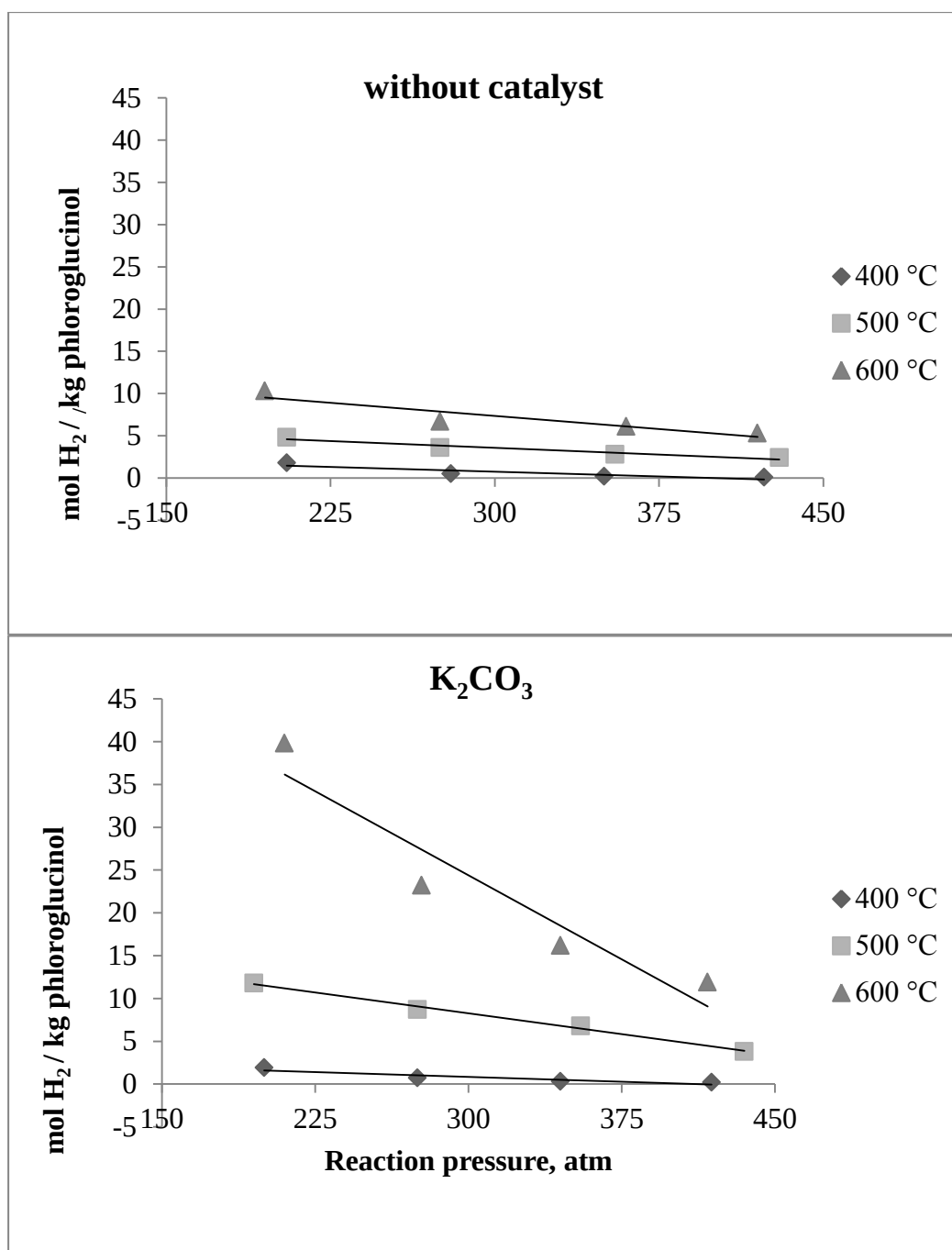


Figure 5.2.14 Pressure effect on hydrogen yield of phloroglucinol hydrothermal gasification in the presence and absence of K₂CO₃.

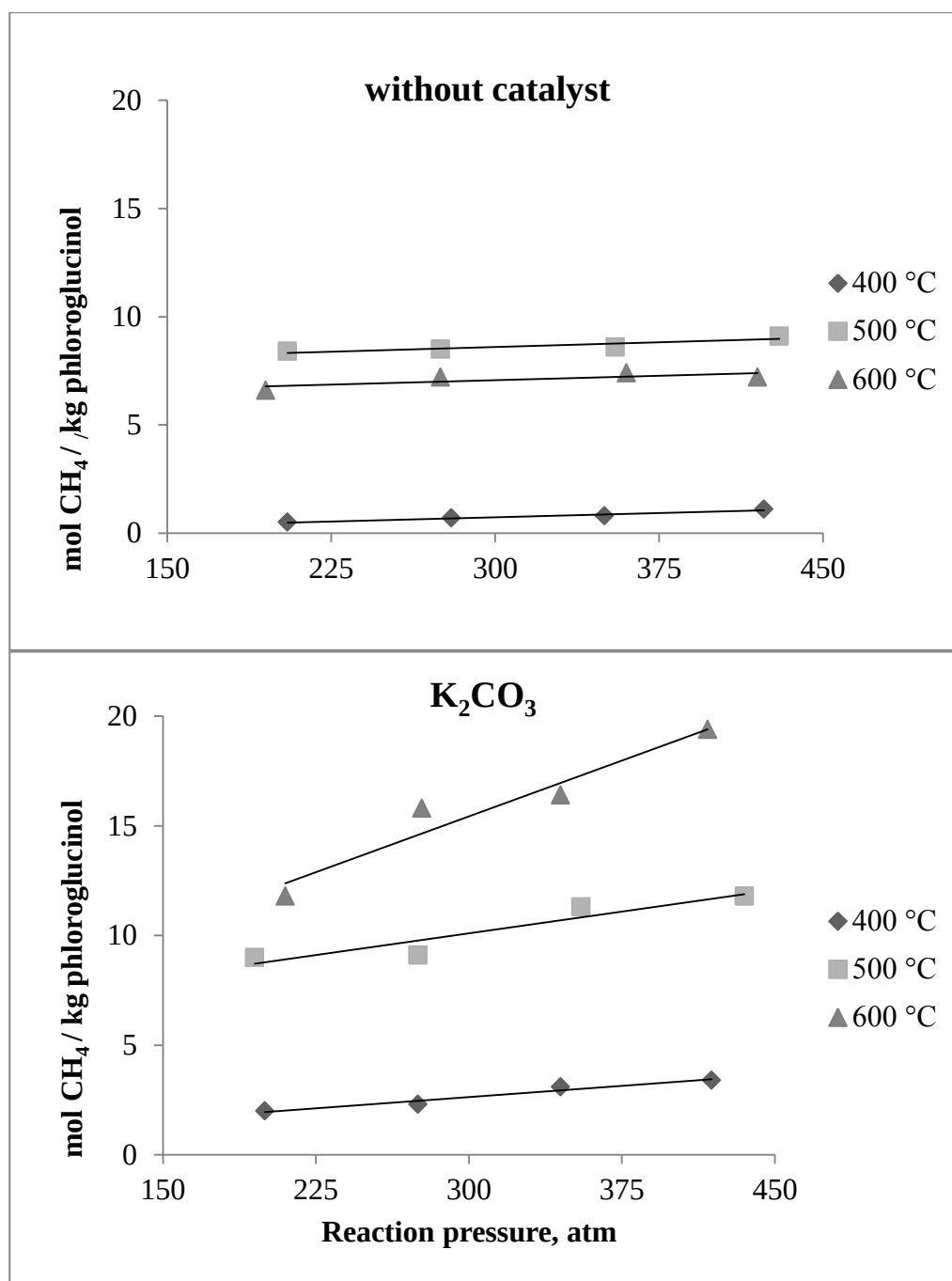


Figure 5.2.15 Pressure effect on methane yield of phloroglucinol hydrothermal gasification in the presence and absence of K₂CO₃.

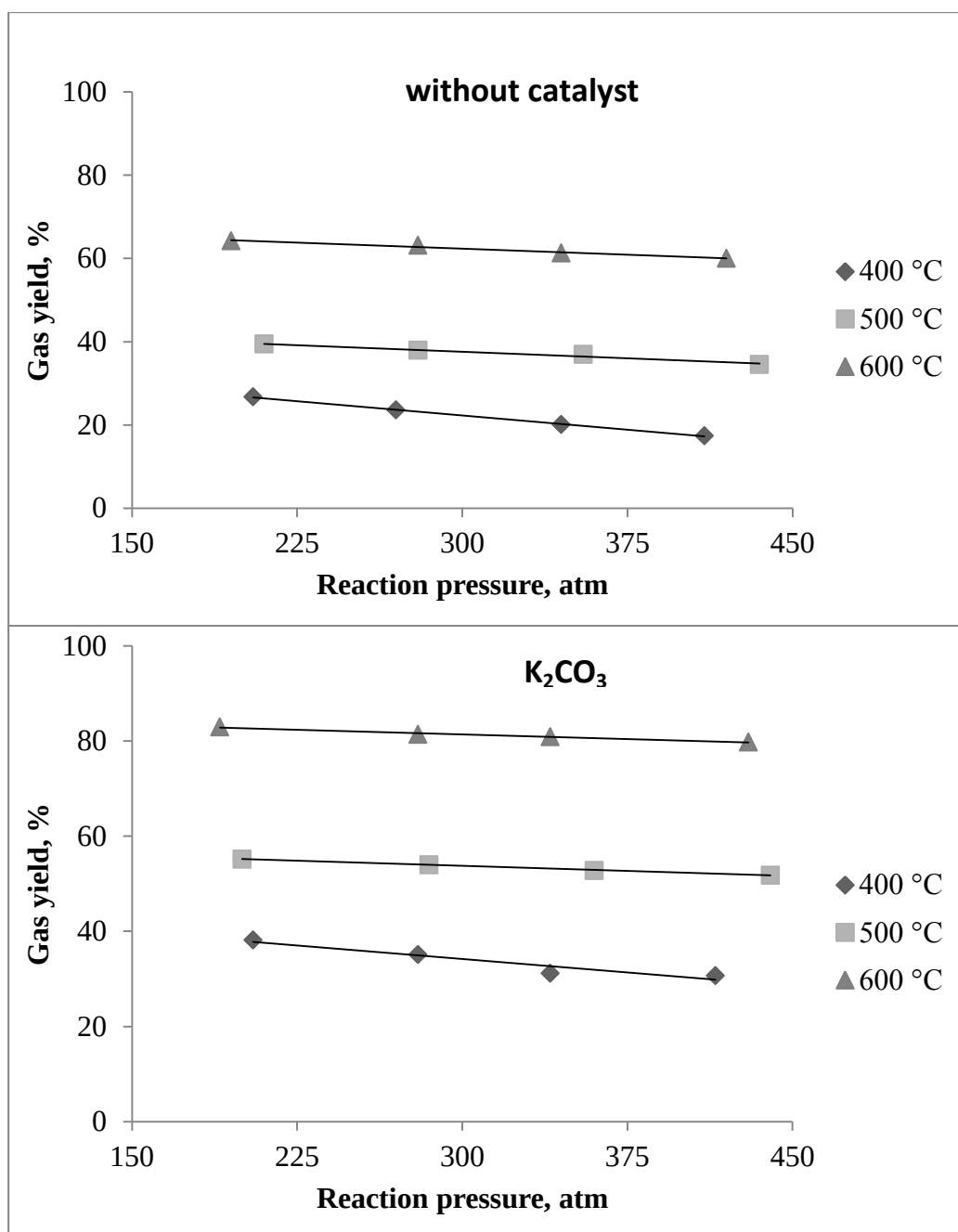


Figure 5.2.16 Pressure effect on gas yield of pyrogallol hydrothermal gasification in the presence and absence of K₂CO₃.

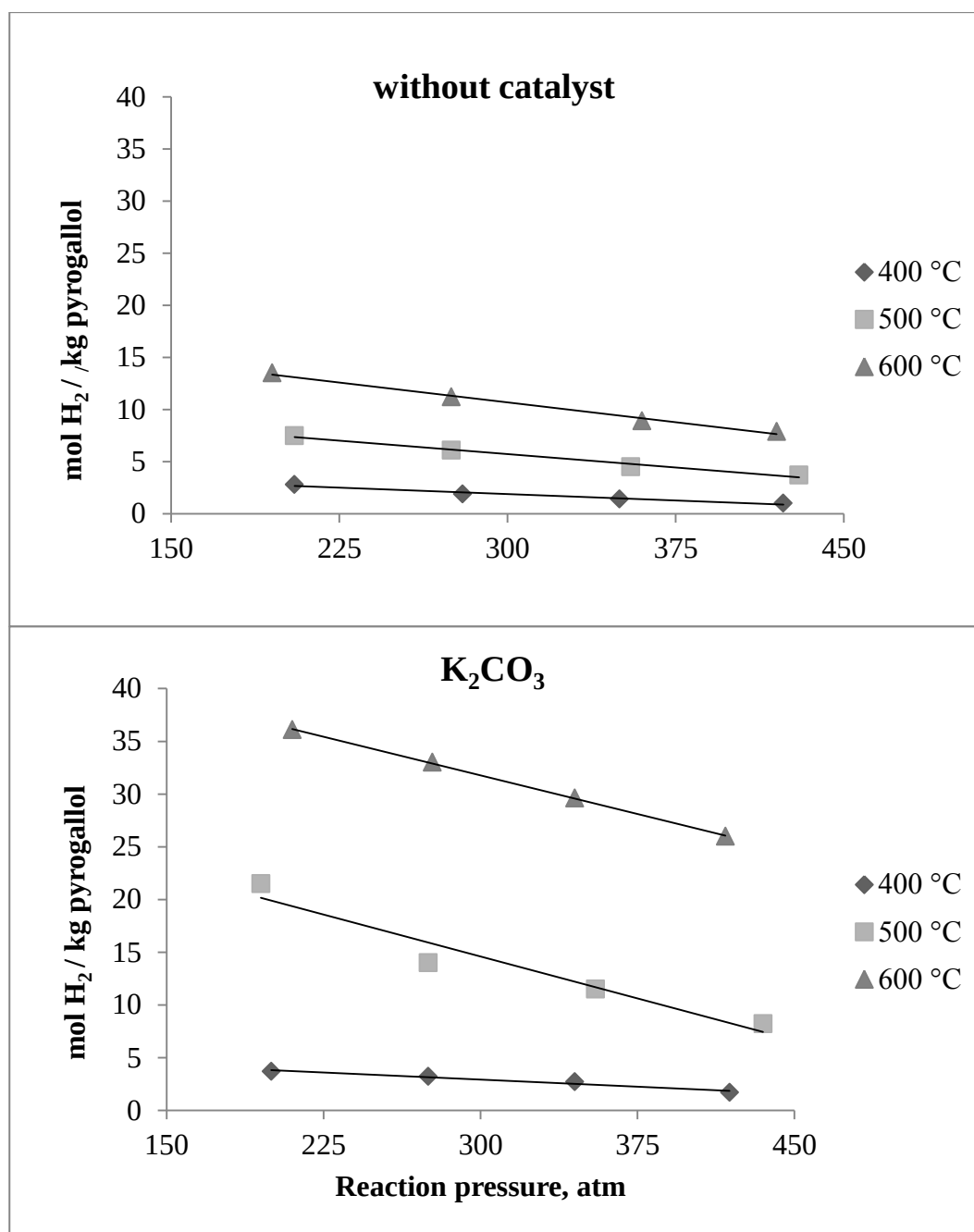


Figure 5.2.17 Pressure effect on hydrogen yield of pyrogallol hydrothermal gasification in the presence and absence of K₂CO₃.

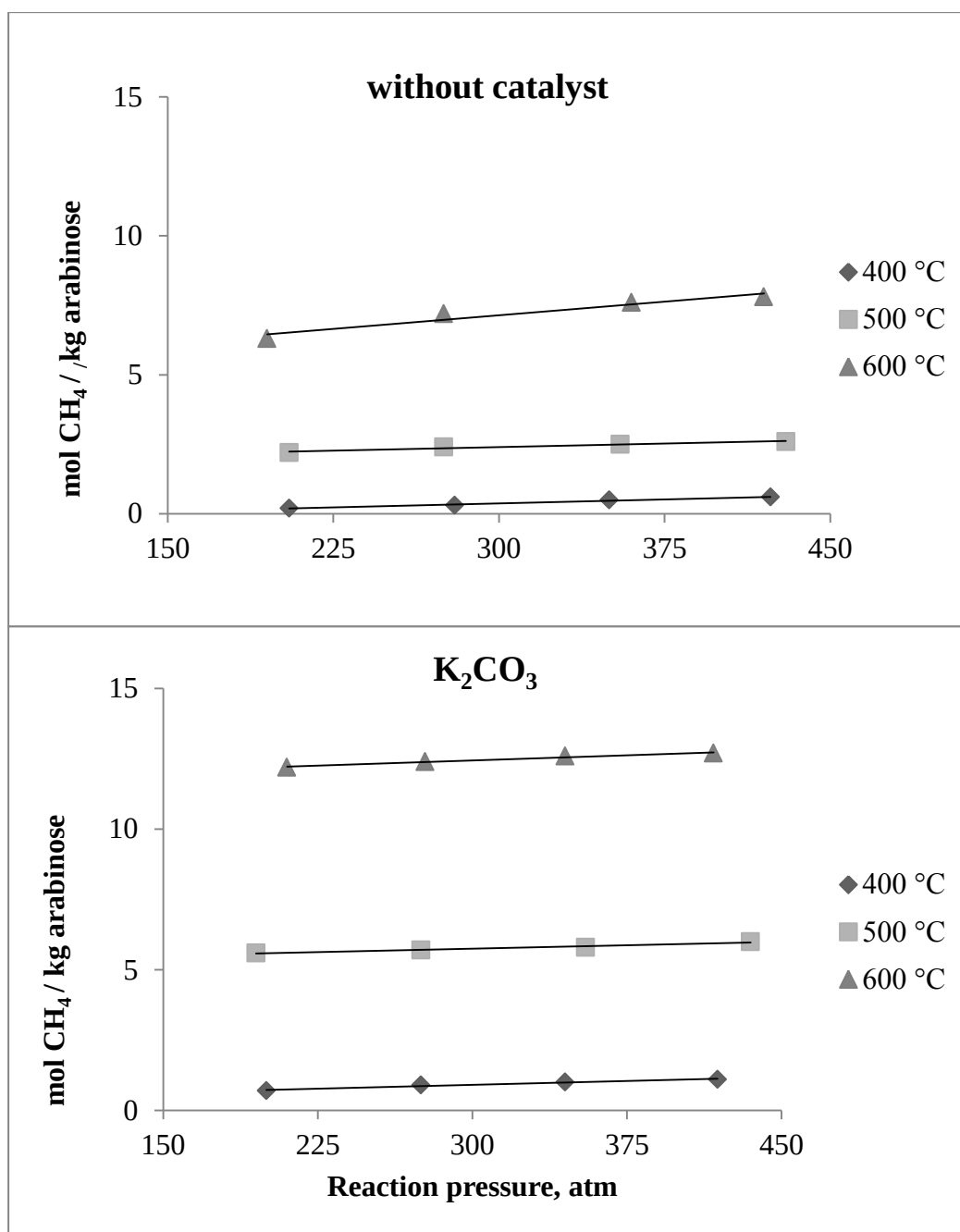


Figure 5.2.18 Pressure effect on methane yield of pyrogallol hydrothermal gasification in the presence and absence of K₂CO₃.

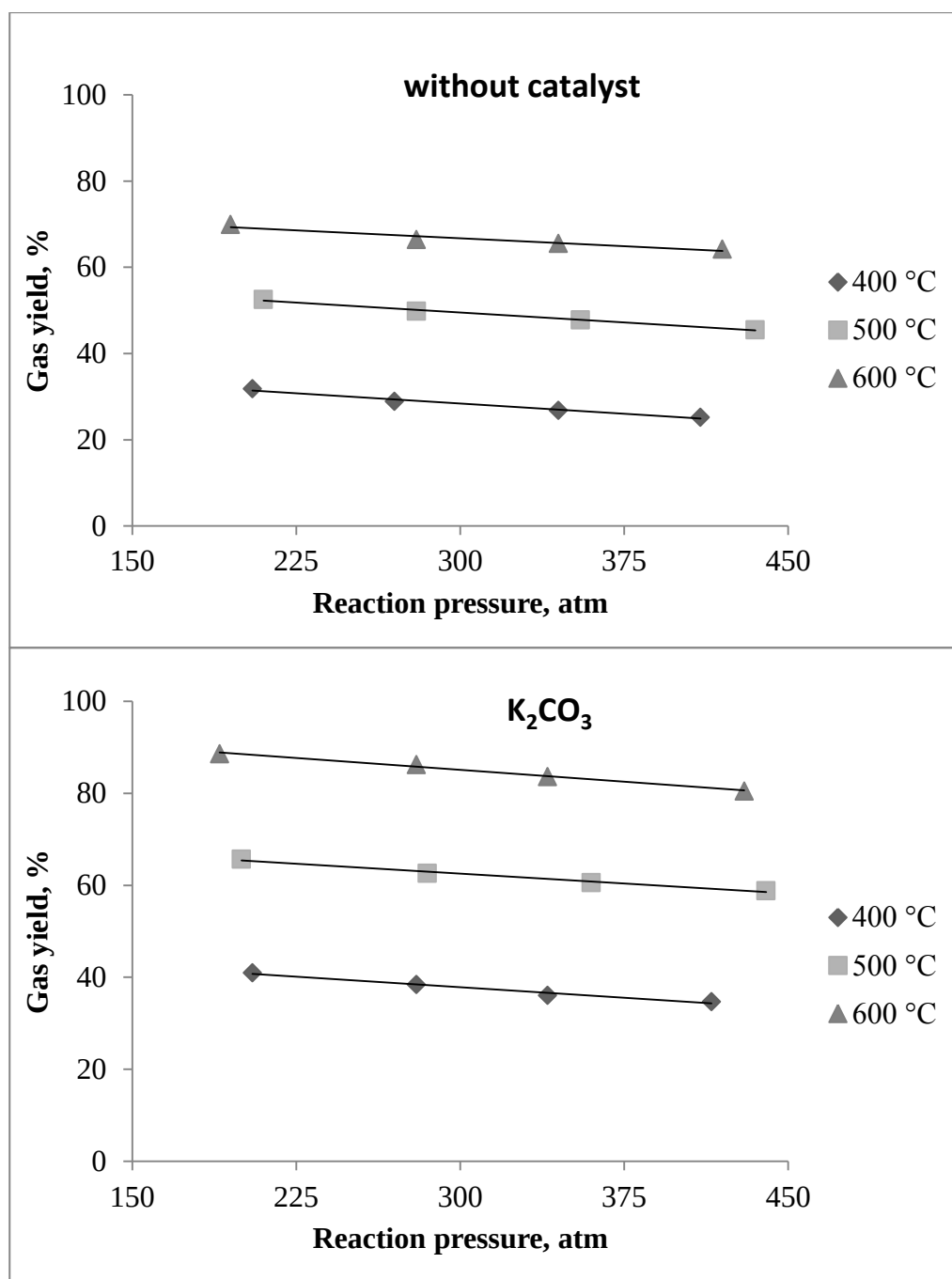


Figure 5.2.19 Pressure effect on gas yield of pectin hydrothermal gasification in the presence and absence of K₂CO₃.

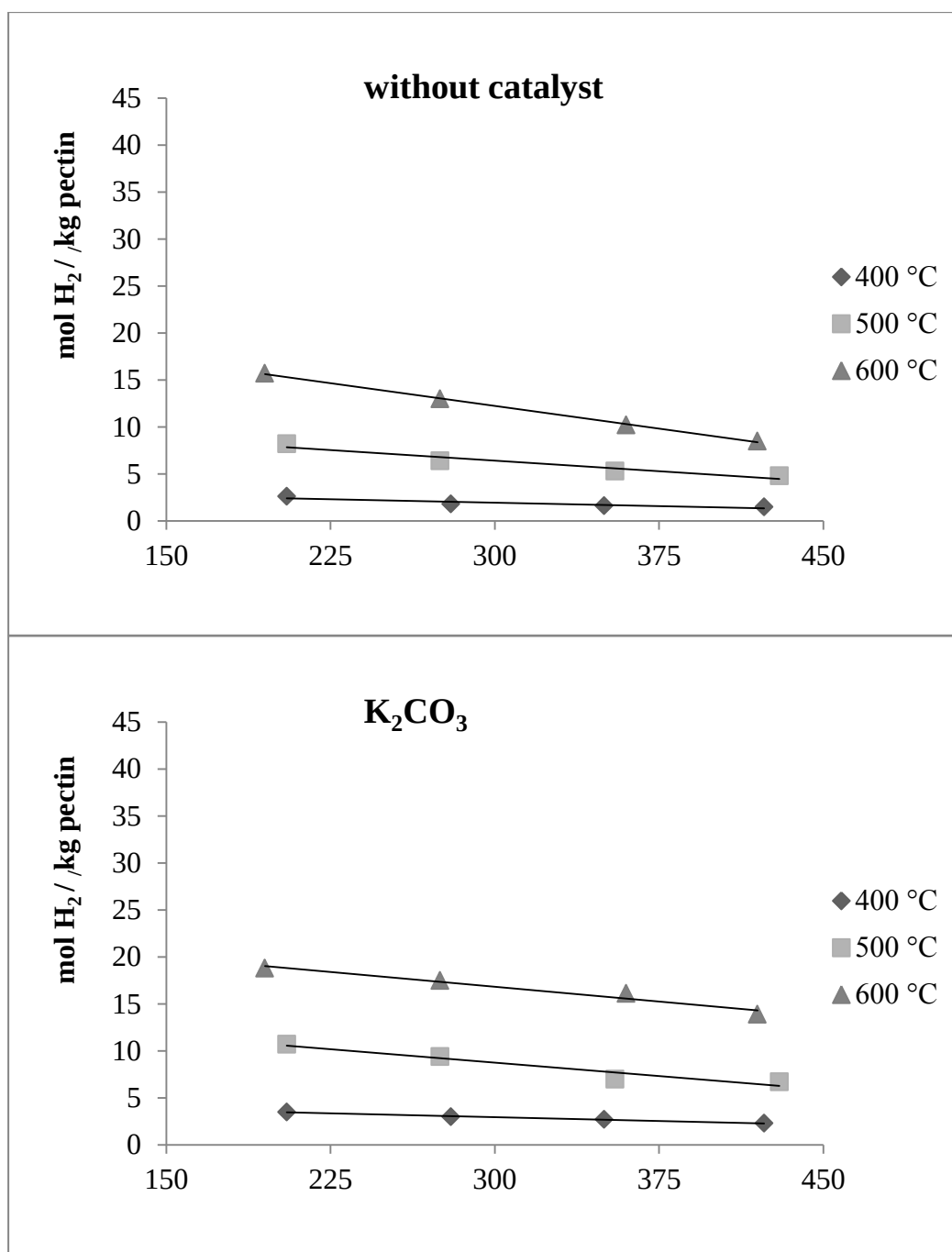


Figure 5.2.20 Pressure effect on hydrogen yield of pectin hydrothermal gasification in the presence and absence of K₂CO₃.

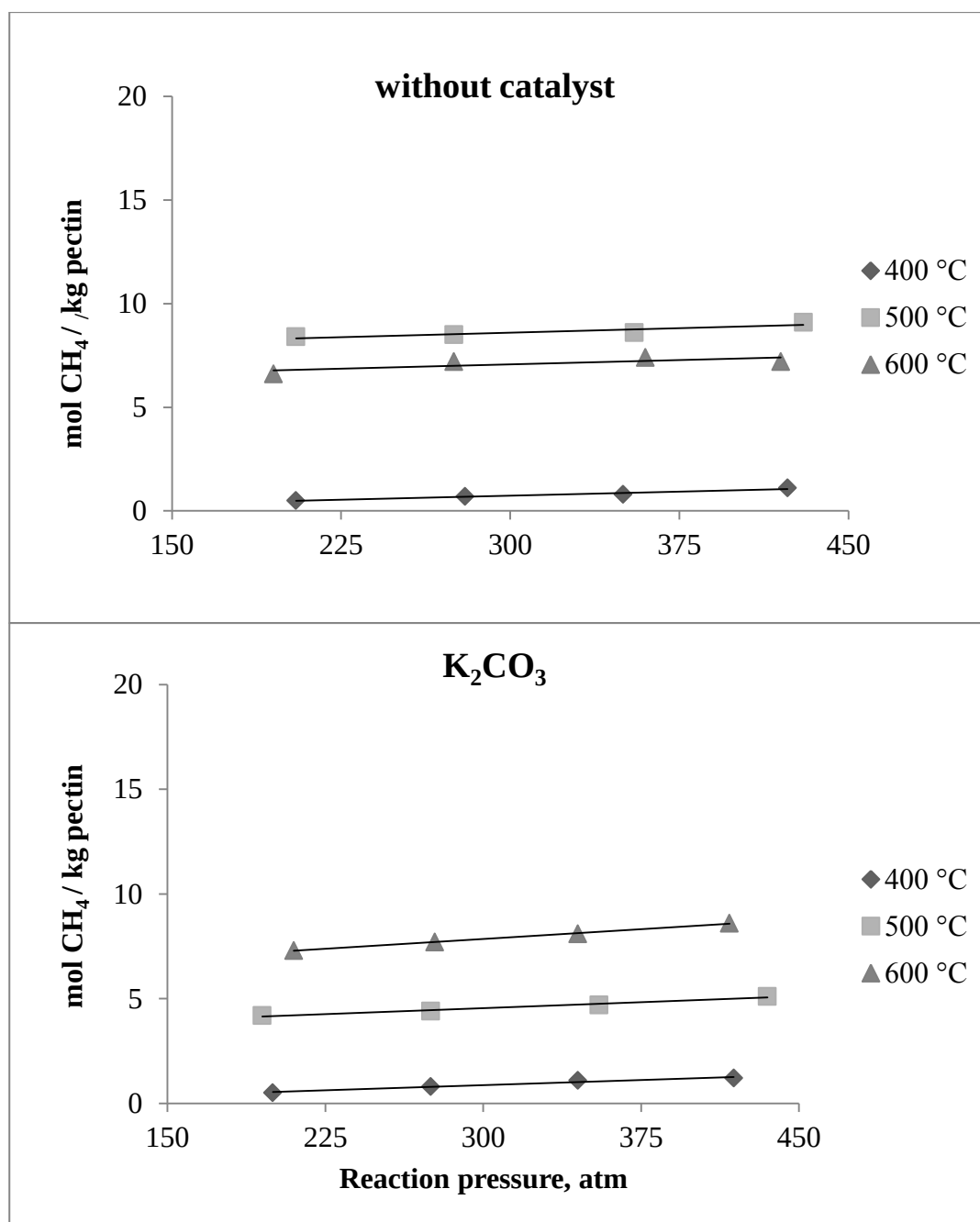
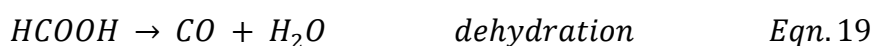
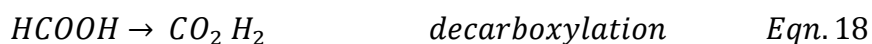


Figure 5.2.21 Pressure effect on methane yield of pectin hydrothermal gasification in the presence and absence of K₂CO₃.

5.3 Influence of Temperature, Pressure and Catalyst on the Liquid Product Distribution

The influence of temperature, pressure and catalyst on liquid product formation during supercritical water gasification of the selected model compounds; xylose, arabinose, tannic acid, gallic acid, phloroglucinol, pyrogallol, pectin and galacturonic acid hydrothermal gasification are given in the Tables 5.3.1-5.3.35. The aqueous products contain large number of compounds, but only key compounds like carboxylic acids (glycolic acid, formic acid, acetic acid), furfurals (furfural, 5-hydroxymethyl furfural, 5-methyl furfural), phenols (o-m-p cresols, phenol, resorcinol, catechol, 3-methoxycatechol, methoxybenzene and 4-methoxyphenol, 2-methoxyphenol and 3-methoxyphenol, 2,6 dimethoxyphenol, 4-methyl guaiacol, 3,4 dimethyl phenol, 3,5 dimethyl phenol and 4-vinyl guaiacol), aldehydes and ketones (formaldehyde, acetaldehyde, acetone, propionaldehyde, 3-methyl-2-cyclo-penten-1-one, 2-cyclo-penten-1-one) were identified to interpret the effects of the reaction conditions.

The variety of the aqueous product contributed to the TOC (Total organic carbon) amount of the liquid phase. TOC value decreases with increasing temperature, as the formed aqueous products degraded into gaseous products. Also in the presence of catalysts, TOC content is lower than in the absence of a catalyst. Aqueous product contained high concentrations of carboxylic acids such as glycolic acid, acetic acid and formic acid which are degradation products of furfural or 5-HMF. The simplest carboxylic acid and formic acid degradation occurs via two pathways, decarboxylation and dehydration (Watanabe et al., 2004, Xianghong et al., 2005). The major products in gas phase CO₂ and H₂ are formed by decarboxylation of formic acid:



Ni/AC and Ru/AC are good catalysts for the formation of carboxylic acids. K₂CO₃ and KOH lead to a decrease of typical acidic intermediates glycolic, acetic and formic acid. This can be due to the formation of potassium formate. Furfural and hydroxy methyl furfural are the principal degradation products of the

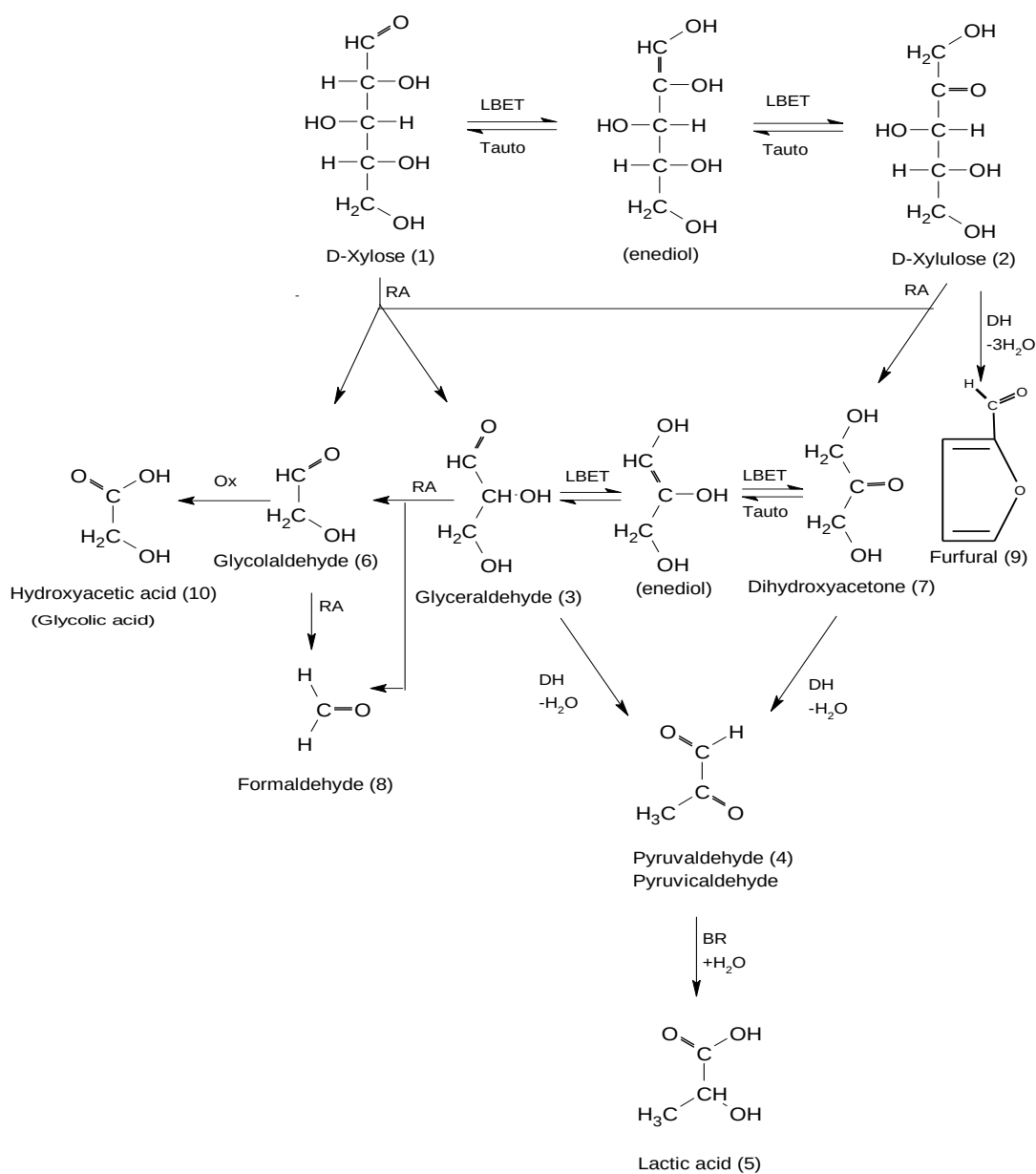
carbohydrates. Protonation one of the hydroxyl groups (2-OH), leads to formation of HMF (Antal et al., 1990). 5-HMF undergoes series reactions of decarbonylation, hydroxylation, tautomerism and cyclization to produce relatively more stable compound 3-methyl-2-cyclopenten-2-one. The 5-HMF yields were low and this may be attributed to the production of furfural from 5-HMF (Aida et al., 2007, Williams et al., 2005). The loss of acetol group from 5-HMF would form furfural, also loss of hydroxyl ion from the acetol group of 5-HMF would produce 5-methylfurfural (5-MF) (Azadi et al., 2011). The aqueous product includes a lot of different phenols. Ortho-, para-, meta-cresols and phenols are analyzed by HPLC and the sum of phenols is detected colorimetrically. Ruthenium seems to force the hydrogenation of phenols and potassium salt catalyzes the formation of phenols.

In order to improve product yield and reduce solid (char and tar) products, degradation pathways of the biomass components in supercritical water conditions were examined. Some researchers have proposed an overall reaction mechanism for the decomposition of glucose. Generally two mechanisms were proposed for the degradation of glucose. The first mechanism involves the formation of 5-hydroxymethylfurfural. The second mechanism involves the hydrolysis of glucose to erythrose (Lee et al., 2002, Williams et al., 2005 and Peterson et al., 2008). Antal and co-workers have proposed a mechanism for xylose degradation (Antal et al., 1990). The structures of glucose and xylose are very similar, there are five hydroxyl groups on the glucose and four hydroxyl groups on the xylose. But their reactivities are so different, it was observed that β -D xylose degrades much faster than β -D glucose. The reactivity of these sugar molecules is dependent on the stability of the carbon cation after the protonated -OH group leaves the ring (Quian et al., 2005). Xylan liquefies at relatively the lower temperatures (180-220°C) in hydrothermal conditions compared to cellulose degradation which takes place at higher temperatures $\sim$ 230°C. In this study the reactivities of glucose and xylose are investigated, to improve reaction conditions for the desired products.

Although the reaction mechanism and kinetics for supercritical water gasification of xylose will likely be similar to that of glucose, differences in decomposition chemistry may affect gasification rates (Goodwin et al., 2010). Antal and co-workers have proposed a mechanism for the protonation of the

glucose and xylose, 2-OH on β -D glucose leads to formation of HMF and 2-OH on β -D xylose leads to formation of furfural (Peterson et al., 2008). 3-OH protonation of xylose leads to the opening of the ring structure and formation of C₁ and C₄ products. In the case of glucose, protonation of 3-OH and 4-OH lead to different degradation products other than HMF (Quian et al., 2005). 1-OH and 6-OH protonations did not lead to any observable reaction. Also there are different degradation products initiated at different hydroxyl groups on the sugar ring glucose or xylose depending on the reaction conditions.

The reaction mechanism for the xylose degradation in supercritical water was presented in the Figure 5.3.1. Since the proposed reaction scheme can not account for all liquid intermediates, Figure 5.3.1 will be introduced aqueous product distribution briefly using the based on the results (Aida et al., 2010, Goodwin et al., 2010). As shown in the Figure 5.3.1 the possible reactions can be seen for xylose in SCW conditions are LBET (Lobry de Bruyn-Alberda Van Ekenstein Transformation), Taut (Tautomerization), RA (Retro Aldol), DH (dehydration), BR (Beuzilic acid rearrangement), Ox (Oxidation). During xylose decomposition in addition to retro-aldol condensation, dehydration to furfural, tautomerisation to xylulose and fragmentation contributed to xylose decomposition. Xylulose produced during the tautomerisation is also dehydrated to furfural by giving three moles of water. Retroaldol condensation was twice faster than both dehydration and tautomerisation and sensitivity towards retro-aldol condensation increased with temperature (Kankanamge et al., 2013). Retro-aldol condensation (RA) of xylose produce glycolaldehyde and glyceraldehyde. Retro-aldol condensation (RA) of xylulose produce dihydroxyacetone. Both glyceraldehyde and dihydroxyacetone can dehydrate into pyruvaldehyde, which further converts into lactic acid via benzilic acid rearrangement. Glycolic acid was produced by oxidation of glycolaldehyde and formaldehyde by retroaldol condensation of glycolaldehyde.



LBET: Lobry de Bruyn-Alberda Van Ekenstein Transformation
 RA: Retro Aldol
 DH: Dehydration
 Taut: Tautomerization
 BR: Beuzilic acid rearrangement
 Ox: oxidation

Figure 5.3.1 Proposed reaction mechanism for gasification of xylose by supercritical water.

The amounts of main aqueous products can be ordered as acetic acid > furfural > formaldehyde. Above the critical temperature of water celluloses and hemicelluloses rapidly decompose to organic acids via a retro-aldol condensation because of free-radical dominated reaction environment (Watanabe et al., 2005, Yu et al., 1998]. So that retro-aldol products were higher than furfural for the 400, 500 and 600°C experiments. The highest retro aldol product acetic acid was 13.90 mol/xylose at 400°C and increased to 19.65 mol/xylose at 600°C. This can be explained by the furfural which is a good candidate for the replacement of formaldehyde (Bobleter, 1994). Below the critical temperature cellulose and hemicellulose sugars dehydrate to furan type compounds, including 5-HMF and furfural because of ionic reaction environment (Goodwin et al., 2010). Also according to the experimental results furfural formation for all experimental conditions was higher than a retro aldol product, formaldehyde. But furfural is a basic component for the production of high polymers, these lead to formation of tar. So that furfural formation to be decreased or suppressed. Using the catalyst of K_2CO_3 has positive effect on the elimination of furfural formation and also furfural can also be decomposed to 5-hydroxymethylfurfural (5-HMF). Disadvantage of K_2CO_3 has been observed by the study of Sinag et al. (2003). They have found that K_2CO_3 increased phenol formation. Phenol formation could have been converted into a non-polar phase (tar), which could have stick inside of the reactor and experimental apparatus. For our experimental results only for 20.0 MPa, it was observed that K_2CO_3 has increased phenol formation at 400, 500 and 600°C. For the other pressures, K_2CO_3 has decreased phenol formation.

Table 5.3.1 Concentrations of major organic compounds identified in liquid product from the gasification of xylose in relation to catalyst and temperature.

Yield (g/kg xylose)	Reaction temperature (°C)	500	600	500	600	500	600
	Reaction pressure (atm)	360	440	345	430	340	440
	Catalyst, % 10	-	-	K ₂ CO ₃	K ₂ CO ₃	KOH	KOH
Carboxylic acids	Glycolic acid	12.83	2.60	1.47	1.05	3.60	9.65
	Formic acid	14.69	4.96	3.41	10.61	11.92	26.74
	Acetic acid	41.15	51.37	33.02	46.97	29.32	34.06
Furfurals	5-Methyl furfural	17.23	36.53	13.11	27.77	24.45	8.74
	5-Hydroxymethyl furfural	9.37	4.63	8.30	1.00	1.17	0.01
	Furfural	40.56	27.30	4.32	5.09	2.24	2.59
Aldehydes and ketones	3-Methyl-2-cyclopentene-1-one	0.22	2.41	0.06	0.00	0.01	0.01
	2-Cyclo-pentan-1-one	0.10	0.06	0.21	0.11	0.13	0.15
	Formaldehyde	0.18	0.14	0.10	0.09	0.08	0.10
	Acetaldehyde	0.52	0.27	0.33	0.24	0.11	0.23
	Acetone and propionaldehyde	0.02	0.01	0.01	0.00	0.00	0.01
Phenols	Phenol	0.02	0.01	0.01	0.00	0.00	0.01
	m- & p-cresol	0.44	0.00	0.80	0.03	1.75	0.02
	o-cresol	0.69	0.36	2.54	0.83	0.47	0.02
	Resorcinol	0.11	1.32	0.18	0.12	0.00	0.08
	Catechol	0.15	0.02	0.13	0.13	0.14	0.03
	3-methoxy catechol	0.00	0.06	0.06	0.05	0.04	0.03
	methoxy benzene+4- methoxy phenol	0.38	0.20	5.54	0.25	4.29	0.14
	2-6 Dimethoxy phenol	0.29	0.16	0.33	0.08	0.22	0.04
	2- methoxy phenol + 3- methoxy phenol	0.08	0.03	0.05	0.05	0.02	0.02
	4-methyl guaiacol	1.18	0.01	1.75	0.03	0.70	0.01
	3,4 methyl phenol	0.22	0.10	0.31	0.52	0.33	0.02
	4-vinyl guaiacol	0.07	0.00	0.38	0.00	0.44	0.01
	3,5 dimethyl phenol	0.14	0.00	0.32	0.00	0.31	0.00
	Total Phenol (colorimetric)	5.84	1.65	7.28	0.61	6.95	0.66

Table 5.3.2 Concentrations of major organic compounds identified in liquid product from the gasification of xylose in relation to catalyst and temperature.

Yield (g/kg xylose)	Reaction temperature (°C)	500	600	500	600
	Reaction pressure (atm)	340	440	325	450
	Catalyst, % 10	AC-Ni	AC-Ni	AC-Ru	AC-Ru
Carboxylic acids	Glycolic acid	22.96	0.22	49.02	13.82
	Formic acid	20.99	2.34	25.55	1.29
	Acetic acid	54.05	16.83	85.01	93.18
Furfurals	5-Methyl furfural	55.76	7.71	136.10	39.91
	5-Hydroxymethyl furfural	15.60	0.12	10.38	0.00
	Furfural	35.26	0.30	31.27	20.86
Aldehydes and ketones	3-Methyl-2-cyclopentene-1-one	0.61	0.00	2.76	0.09
	2-Cyclo-pentan-1-one	0.12	0.01	0.26	0.27
	Formaldehyde	0.40	0.02	0.05	0.06
	Acetaldehyde	1.47	0.02	0.17	0.40
	Acetone and propionaldehyde	22.90	1.27	15.37	3.39
Phenols	Phenol	0.01	0.00	0.00	0.00
	m- & p-cresol	0.34	0.00	0.00	0.00
	o-cresol	0.07	0.00	0.00	0.00
	Resorcinol	1.68	0.00	1.67	1.04
	Catechol	0.14	0.00	0.00	0.01
	3-methoxy catechol	0.04	0.03	0.00	0.01
	methoxy benzene+4- methoxy phenol	2.86	0.04	0.05	0.12
	2-6 Di methoxy phenol	0.34	0.00	0.06	0.03
	2- methoxy phenol + 3- methoxy phenol	0.06	0.00	0.03	0.02
	4-methyl guaiacol	1.10	0.00	0.25	0.00
	3,4 methyl phenol	0.38	0.00	0.03	0.00
	4-vinyl guaiacol	0.08	0.01	0.03	0.00
	3,5 dimethyl phenol	0.12	0.00	0.03	0.00
	Total Phenol (colorimetric)	5.62	0.39	2.37	1.21

Table 5.3.3 Concentrations of major organic compounds identified in liquid product from the gasification of xylose in relation to pressure for the reaction temperature of 400°C.

Yield (g/kg xylose)	Reaction pressure	20.5	28.0	35.0	42.3	20.0	27.5	34.5	41.9
	Catalyst, % 10	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Carboxylic acids		14.80	17.55	15.48	0.68	10.14	2.64	19.76	7.52
	Glycolic acid	14.73	24.25	10.58	0.13	11.29	3.00	24.19	8.40
	Formic acid	92.60	67.85	47.01	22.94	77.97	79.72	87.90	80.36
	Acetic acid								
Furfurals	5-Methyl furfural	49.06	46.02	18.05	14.75	48.55	75.50	46.21	47.34
	5-Hydroxymethyl furfural	31.32	6.35	10.66	5.55	14.00	10.52	36.78	15.66
	Furfural	14.80	28.83	16.42	0.51	1.85	2.23	2.85	0.21
Aldehydes and ketones	3-Methyl-2-cyclopentene-1-one	0.28	0.64	2.00	1.12	0.99	1.07	0.94	1.15
	2-Cyclo-pentan-1-one	0.51	0.73	4.30	2.28	0.47	0.39	0.47	0.27
	Formaldehyde	0.50	0.36	0.29	0.01	0.18	0.07	0.03	0.05
	Acetaldehyde	4.22	2.83	4.49	2.46	2.50	2.69	2.03	1.60
	Acetone and propionaldehyde	1.53	6.25	0.01	1.00	1.66	3.84	0.98	3.87
Phenols	Phenol	0.01	0.03	0.05	0.01	0.02	0.01	0.02	0.00
	m-& p-cresol	1.06	0.76	1.12	0.18	2.51	1.30	0.83	0.51
	o-cresol	3.99	0.14	2.92	0.30	1.86	0.45	2.81	0.02
	Resorcinol	0.90	1.52	1.22	0.03	0.09	0.13	0.06	0.00
	Catechol	1.01	1.00	3.01	1.47	0.32	0.28	0.39	0.74
	3-methoxy catechol	0.56	0.05	0.09	0.00	0.12	0.05	0.17	0.02
	methoxy benzene+4- methoxy phenol	4.61	2.17	1.38	1.07	4.58	3.63	1.43	3.58
	2-6 Di methoxy phenol	0.74	0.23	0.40	0.13	0.35	0.36	0.36	0.22
	2- methoxy phenol + 3- methoxy phenol	0.16	0.05	0.11	0.01	0.19	0.07	0.08	0.02
	4-methyl guaiacol	0.92	0.18	0.76	0.01	1.54	1.35	1.18	0.82
	3,4 methyl phenol	0.01	0.01	0.05	0.08	0.26	0.26	0.34	0.69
	4-vinyl guaiacol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	3,5 dimethyl phenol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Total Phenol (colorimetric)	6.25	6.06	6.06	5.61	8.03	5.23	5.23	5.23

Table 5.3.4 Concentrations of major organic compounds identified in liquid product from the gasification of xylose in relation to pressure for the reaction temperature of 500°C.

Yield (g/kg xylose)	Reaction pressure	20.5	28.0	35.0	42.3	20.0	27.5	34.5	41.9
	Catalyst, % 10	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Carboxylic acids	Glycolic acid	43.54	5.94	19.16	9.63	13.17	0.78	3.87	18.85
	Formic acid	17.86	12.68	13.65	6.84	12.28	7.78	5.86	22.05
	Acetic acid	127.53	23.80	16.77	9.86	31.26	27.01	19.43	48.01
Furfurals	5-Methyl furfural	77.37	20.17	22.69	7.63	42.79	20.36	37.60	36.98
	5-Hydroxymethyl furfural	9.54	8.78	17.07	11.55	6.63	10.87	9.74	13.11
	Furfural	55.53	6.25	13.18	4.08	2.93	1.96	2.00	0.82
Aldehydes and ketones	3-Methyl-2-cyclopentene-1-one	0.07	0.03	0.01	0.01	0.10	0.05	0.28	0.01
	2-Cyclo-pentan-1-one	0.02	0.00	0.02	0.03	0.02	0.01	0.02	0.02
	Formaldehyde	0.81	0.93	0.78	1.01	0.05	2.11	2.93	1.92
	Acetaldehyde	3.90	0.32	0.14	1.38	0.60	0.39	2.48	0.19
	Acetone and propionaldehyde	0.43	0.16	0.19	0.11	0.31	0.20	0.29	0.15
Phenols	Phenol	3.12	0.26	0.69	0.24	0.21	0.13	0.09	0.04
	m- & p-cresol	0.17	0.00	0.43	0.28	0.22	0.15	0.16	0.07
	o-cresol	0.03	0.00	0.04	0.03	0.09	0.09	0.04	0.16
	Resorcinol	3.80	5.99	4.84	12.58	5.26	5.57	6.04	5.72
	Catechol	0.15	0.01	0.13	0.01	0.14	0.06	0.04	0.02
	3-methoxy catechol	0.02	0.01	0.03	0.03	0.02	0.01	0.00	0.00
	methoxy benzene+4- methoxy phenol	0.84	0.21	0.45	1.81	0.03	0.21	0.14	0.13
	2-6 Di methoxy phenol	0.11	0.00	0.19	0.14	0.18	0.66	0.33	0.28
	2- methoxy phenol + 3- methoxy phenol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	4-methyl guaiacol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	3,4 methyl phenol	1.05	0.10	0.23	0.06	0.22	0.29	0.34	0.39
	4-vinyl guaiacol	1.12	0.10	0.34	0.12	0.12	0.04	0.22	0.25
	3,5 dimethyl phenol	8.14	2.59	3.94	2.65	2.19	2.28	0.75	1.36
	Total Phenol (colorimetric)	5.21	7.97	7.97	8.61	8.20	1.79	1.79	7.97

Table 5.3.5 Concentrations of major organic compounds identified in liquid product from the gasification of xylose in relation to pressure for the reaction temperature of 600°C.

Yield (g/kg xylose)	Reaction pressure	20.5	28.0	35.0	42.3	20.0	27.5	34.5	41.9
	Catalyst, % 10	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Carboxylic acids	Glycolic acid	32.83	18.43	38.67	15.24	10.26	5.70	8.56	0.98
	Formic acid	24.30	19.95	26.85	10.25	14.97	12.88	14.90	20.89
	Acetic acid	110.89	92.29	65.67	23.05	73.23	26.89	57.73	44.49
Furfurals	5-Methyl furfural	71.50	51.30	36.55	19.11	41.59	28.45	25.38	18.17
	5-Hydroxymethyl furfural	39.44	5.57	1.02	0.55	5.37	2.80	7.93	2.57
	Furfural	34.03	18.83	44.29	17.29	2.15	1.16	1.14	0.54
Aldehydes and ketones	3-Methyl-2-cyclopentene-1-one	0.19	0.03	0.16	0.01	0.00	0.02	0.13	0.01
	2-Cyclo-pentan-1-one	0.01	0.01	0.02	0.00	0.00	0.00	0.00	0.01
	Formaldehyde	0.19	0.10	0.39	0.11	0.00	0.00	0.08	0.00
	Acetaldehyde	0.03	0.00	0.00	0.00	0.00	0.00	0.65	0.27
	Acetone and propionaldehyde	0.39	0.13	0.83	0.07	0.13	0.05	0.45	0.15
Phenols	Phenol	1.47	0.86	2.33	0.68	0.12	0.01	0.02	0.05
	m- & p-cresol	0.49	0.08	0.02	0.01	0.26	0.09	0.43	0.07
	o-cresol	0.11	0.16	0.05	0.02	0.14	0.04	0.14	0.09
	Resorcinol	3.02	3.03	1.66	1.61	0.15	0.29	0.41	0.72
	Catechol	0.01	0.01	0.16	0.00	0.01	0.01	0.19	0.00
	3-methoxy catechol	0.01	0.03	0.15	0.00	0.00	0.00	0.07	0.01
	methoxy benzene+4- methoxy phenol	0.01	0.00	0.07	0.03	0.00	0.00	0.00	0.00
	2-6 Di methoxy phenol	0.00	0.00	0.00	0.34	0.00	0.00	0.00	0.00
	2- methoxy phenol + 3- methoxy phenol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	4-methyl guaiacol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	3,4 methyl phenol	0.53	0.22	0.88	0.16	0.04	0.17	0.03	0.14
	4-vinyl guaiacol	1.57	0.38	2.67	0.17	0.10	0.18	0.48	0.15
	3,5 dimethyl phenol	0.16	3.67	6.97	3.07	0.33	0.54	0.58	0.29
	Total Phenol (colorimetric)	5.25	4.40	4.40	2.81	1.92	5.23	5.23	0.70

Table 5.3.6 Concentrations of major organic compounds identified in liquid product from the gasification of arabinose in relation to catalyst and temperature.

Yield (g/kg arabinose)	Reaction temperature (°C)	500	600	500	600	500	600
	Reaction pressure (atm)	350	440	370	440	340	480
	Catalyst, % 10	-	-	K ₂ CO ₃	K ₂ CO ₃	KOH	KOH
Carboxylic acids	Glycolic acid	16.51	4.14	3.17	1.18	0.77	0.38
	Formic acid	14.59	2.77	12.76	20.87	22.11	11.86
	Acetic acid	58.48	42.46	26.89	111.50	29.92	21.26
Furfurals	5-Methyl furfural	0.00	29.21	13.18	80.00	11.90	7.94
	5-Hydroxymethyl furfural	2.10	0.00	3.28	3.69	1.04	0.83
	Furfural	34.15	8.04	4.21	1.52	2.10	1.46
Aldehydes and ketones		2.96	0.00	0.00	0.00	0.00	0.00
	3-Methyl-2-cyclopentene-1-one						
	2-Cyclo-pentan-1-one	0.14	0.25	0.23	0.07	0.13	0.16
	Formaldehyde	0.27	0.01	0.03	0.05	0.22	0.03
	Acetaldehyde	0.49	1.04	0.34	0.27	0.25	0.44
	Acetone and propionaldehyde	30.63	2.86	7.73	1.71	2.78	10.93
Phenols	Phenol	0.02	0.01	0.01	0.00	0.00	0.00
	m- & p-cresol	0.46	0.00	0.84	0.00	0.02	1.83
	o-cresol	0.96	0.00	0.60	0.00	0.00	1.01
	Resorcinol	1.83	0.48	0.19	0.04	0.05	0.04
	Catechol	0.13	0.22	0.19	0.10	0.10	0.11
	3-methoxy catechol	0.04	0.04	0.07	0.04	0.01	0.03
	methoxy benzene+4- methoxy phenol	4.17	1.73	5.35	0.24	0.13	5.13
	2-6 Di methoxy phenol	0.32	0.11	0.28	0.05	0.04	0.24
	2- methoxy phenol + 3- methoxy phenol	0.06	0.07	0.05	0.03	0.02	0.02
	4-methyl guaiacol	1.30	0.02	1.20	0.00	0.01	1.81
	3,4 methyl phenol	0.25	0.05	0.29	0.25	0.01	0.39
	4-vinyl guaiacol	0.07	0.01	0.37	0.00	0.00	0.44
	3,5 dimethyl phenol	0.18	0.00	0.34	0.00	0.00	0.35
	Total Phenol (colorimetric)	6.45	2.15	6.95	0.61	0.55	7.44

Table 5.3.7 Concentrations of major organic compounds identified in liquid product from the gasification of arabinose in relation to catalyst and temperature.

Yield (g/kg arabinose)	Reaction temperature (°C)	500	600	500	600
	Reaction pressure (atm) Catalyst, % 10	350 AC-Ni	445 AC-Ni	356 AC-Ru	443 AC-Ru
Carboxylic acids	Glycolic acid	16.43	3.94	26.94	20.15
	Formic acid	12.98	4.21	17.08	27.81
	Acetic acid	139.98	88.23	195.13	21.20
Furfurals	5-Methyl furfural	48.26	67.22	170.74	22.49
	5-Hydroxymethyl furfural	27.05	1.03	1.76	0.00
	Furfural	26.22	7.88	26.86	3.97
Aldehydes and ketones	3-Methyl-2-cyclopentene-1-one	2.15	0.06	0.00	0.00
	2-Cyclo-pentan-1-one	0.11	0.16	0.40	0.03
	Formaldehyde	0.20	0.15	0.17	0.05
	Acetaldehyde	0.17	0.18	0.39	0.04
	Acetone and propionaldehyde	18.28	3.81	6.68	1.18
Phenols	Phenol	0.01	0.00	0.01	0.00
	m-& p-cresol	0.41	0.01	0.07	0.00
	o-cresol	1.11	0.03	0.35	0.16
	Resorcinol	1.58	0.28	1.19	0.08
	Catechol	0.10	0.03	0.03	0.00
	3-methoxy catechol	0.05	0.06	0.02	0.00
	methoxy benzene+4- methoxy phenol	3.31	0.13	0.10	0.01
	2-6 Di methoxy phenol	0.26	0.17	0.04	0.00
	2- methoxy phenol + 3- methoxy phenol	0.06	0.00	0.02	0.00
	4-methyl guaiacol	1.55	0.00	0.00	0.12
	3,4 methyl phenol	0.20	0.11	0.01	0.00
	4-vinyl guaiacol	0.06	0.03	0.02	0.00
	3,5 dimethyl phenol	0.18	0.00	0.00	0.00
	Total Phenol (colorimetric)	5.84	2.26	1.21	1.16

Table 5.3.8 Concentrations of major organic compounds identified in liquid product from the gasification of arabinose in relation to pressure for the reaction temperature of 400°C.

Yield (g/kg arabinose)	Reaction pressure	205	270	345	410	205	280	340	415
	Catalyst, % 10	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Carboxylic acids									
	Glycolic acid	9.38	5.64	2.77	3.96	3.73	8.85	0.61	3.14
	Formic acid	23.47	14.11	4.59	0.06	10.97	28.04	3.82	4.34
	Acetic acid	91.30	67.23	43.22	2.66	51.39	140.90	93.60	76.30
Furfurals									
	5-Methyl furfural	25.00	54.98	20.05	0.02	21.08	103.79	65.82	43.03
	5-Hydroxymethyl furfural	151.22	62.43	34.99	142.77	9.43	225.71	18.93	57.24
	Furfural	40.72	26.98	9.17	1.30	0.48	1.90	1.74	0.09
Aldehydes and ketones									
	3-Methyl-2-cyclopentene-1-one	3.40	3.49	2.93	0.42	1.10	1.54	1.47	0.00
	2-Cyclo-pentan-1-one	1.87	3.79	3.55	3.96	0.34	0.71	0.41	0.34
	Formaldehyde	0.47	0.16	0.06	0.09	0.15	0.03	0.07	0.05
	Acetaldehyde	4.72	3.02	3.78	4.07	1.94	2.57	1.75	1.24
	Acetone and propionaldehyde	19.16	4.85	1.22	1.67	16.61	2.08	1.99	2.01
Phenols									
	Phenol	0.09	0.10	0.02	0.59	0.01	0.00	0.01	0.00
	m- & p-cresol	0.00	0.00	0.00	0.38	0.04	0.00	4.09	3.88
	o-cresol	0.00	0.00	0.00	0.07	1.88	0.00	0.00	0.00
	Resorcinol	1.95	1.51	0.42	0.06	0.00	0.05	0.07	0.01
	Catechol	2.06	2.59	2.54	2.66	0.05	0.53	0.72	1.02
	3-methoxy catechol	0.03	0.07	0.02	0.02	0.03	0.25	0.03	0.26
	methoxy benzene+4- methoxy phenol	0.54	1.84	0.67	1.30	3.22	1.12	1.75	2.07
	2-6 Di methoxy phenol	0.38	0.49	0.16	0.42	0.29	0.45	0.41	0.24
	2- methoxy phenol + 3-methoxy phenol	0.24	0.27	0.00	0.06	0.13	0.06	0.12	0.02
	4-methyl guaiacol	0.77	0.75	0.19	0.59	1.66	1.76	1.53	0.88
	3,4 methyl phenol	0.55	1.04	0.15	0.38	0.93	1.67	0.82	0.00
	4-vinyl guaiacol	0.01	0.01	0.03	0.07	0.69	0.19	0.02	0.05
	3,5 dimethyl phenol	0.06	0.63	0.29	0.30	0.34	0.71	0.51	0.34
	Total Phenol (colorimetric)	6.25	6.06	6.06	5.61	8.03	5.23	5.23	5.23

Table 5.3.9 Concentrations of major organic compounds identified in liquid product from the gasification of arabinose in relation to pressure for the reaction temperature of 500°C.

Yield (g/kg arabinose)	Reaction pressure	210	280	355	435	200	285	360	440
	Catalyst, % 10	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Carboxylic acids									
	Glycolic acid	5.02	4.98	9.63	0.10	0.00	0.00	0.51	0.28
	Formic acid	9.30	6.56	27.03	0.77	3.31	21.16	6.23	16.01
	Acetic acid	76.43	74.76	80.14	0.29	70.61	16.01	28.50	17.90
Furfurals									
	5-Methyl furfural	37.16	17.29	40.83	0.01	0.00	2.73	7.55	11.17
	5-Hydroxymethyl furfural	26.44	24.08	19.24	13.17	4.60	9.53	19.06	17.48
	Furfural	19.28	13.11	10.17	5.67	2.91	2.01	3.48	2.50
Aldehydes and ketones									
	3-Methyl-2-cyclopentene-1-one	0.00	0.00	0.00	0.08	0.01	0.27	0.04	0.01
	2-Cyclo-pentan-1-one	0.39	0.19	0.12	0.10	0.25	0.26	0.19	0.08
	Formaldehyde	0.43	0.17	0.14	0.08	0.06	0.09	0.23	0.22
	Acetaldehyde	1.28	0.88	0.47	0.60	0.13	0.23	1.28	0.58
	Acetone and propionaldehyde	5.08	2.52	18.56	4.21	0.81	4.39	2.35	2.66
Phenols									
	Phenol	0.00	0.02	0.01	0.29	0.01	0.01	0.00	0.00
	m- & p-cresol	0.00	0.00	0.00	0.00	0.05	3.87	3.18	2.35
	o-cresol	0.00	0.00	0.00	0.07	0.26	3.61	3.72	0.10
	Resorcinol	0.79	0.52	0.40	0.77	0.18	0.11	0.19	0.11
	Catechol	0.11	0.09	0.04	0.29	0.00	0.22	0.12	0.07
	3-methoxy catechol	0.01	0.03	0.06	0.01	0.03	0.05	0.02	0.02
	methoxy benzene+4- methoxy phenol	6.04	5.01	6.81	5.67	4.38	6.52	5.97	5.17
	2-6 Di methoxy phenol	0.08	0.01	0.12	0.08	0.08	0.09	0.04	0.04
	2- methoxy phenol + 3-methoxy phenol	0.10	0.02	0.03	0.02	0.03	0.03	0.00	0.01
	4-methyl guaiacol	1.33	1.68	1.51	0.29	1.05	2.03	1.75	0.00
	3,4 methyl phenol	0.26	0.29	0.31	0.00	0.54	1.01	0.40	0.25
	4-vinyl guaiacol	0.05	0.02	0.36	0.07	0.47	1.08	0.67	0.99
	3,5 dimethyl phenol	0.46	1.29	0.58	0.44	0.25	3.39	0.01	0.00
	Total Phenol (colorimetric)	5.21	7.97	7.97	8.61	8.20	1.79	1.79	7.97

Table 5.3.10 Concentrations of major organic compounds identified in liquid product from the gasification of arabinose in relation to pressure for the reaction temperature of 600°C.

Yield (g/kg arabinose)	Reaction pressure	195	280	345	420	190	280	340	430
	Catalyst, % 10	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Carboxylic acids									
	Glycolic acid	7.60	6.05	3.06	0.04	1.46	0.00	0.00	0.58
	Formic acid	12.04	9.87	11.04	0.65	0.00	7.32	7.83	17.26
	Acetic acid	83.93	41.44	72.84	0.00	58.88	34.71	20.63	44.29
Furfurals									
	5-Methyl furfural	40.51	20.74	39.29	0.03	31.31	19.13	14.08	23.04
	5-Hydroxymethyl furfural	27.80	21.08	0.00	10.48	0.00	0.00	0.00	5.15
	Furfural	30.09	18.98	15.56	3.85	3.28	0.23	0.72	3.52
Aldehydes and ketones									
	3-Methyl-2-cyclopentene-1-one	0.00	0.00	0.00	0.04	0.20	0.01	0.00	0.00
	2-Cyclo-pentan-1-one	0.31	0.09	0.16	0.04	0.75	0.01	0.04	0.08
	Formaldehyde	0.68	0.23	0.51	0.10	1.51	0.09	0.17	0.27
	Acetaldehyde	1.08	0.64	0.36	0.80	0.43	0.05	0.02	0.56
	Acetone and propionaldehyde	5.71	3.08	2.65	5.09	0.76	0.08	0.13	0.62
Phenols									
	Phenol	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.02
	m-& p-cresol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	o-cresol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Resorcinol	1.02	0.65	0.57	0.65	0.01	0.01	0.00	0.18
	Catechol	0.10	0.01	0.05	0.00	0.08	0.01	0.02	0.05
	3-methoxy catechol	0.03	0.01	0.04	0.03	0.02	0.01	0.03	0.06
	methoxy benzene+4- methoxy phenol	3.50	3.05	4.15	3.85	0.42	0.16	1.18	0.55
	2-6 Di methoxy phenol	0.08	0.05	0.00	0.04	0.05	0.00	0.07	0.17
	2- methoxy phenol + 3-methoxy phenol	0.05	0.05	0.04	0.01	0.00	0.00	0.00	0.00
	4-methyl guaiacol	0.01	0.01	0.01	0.00	0.00	0.24	0.02	0.01
	3,4 methyl phenol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	4-vinyl guaiacol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	3,5 dimethyl phenol	0.00	0.00	0.00	0.00	0.75	0.00	0.00	0.00
	Total Phenol (colorimetric)	5.25	4.40	4.40	2.81	1.92	5.23	5.23	0.70

Table 5.3.11. Concentrations of major organic compounds identified in liquid product from the gasification of tannic acid in relation to catalyst and temperature.

Yield (g/kg tannic acid)	Reaction temperature (°C)	400	500	600	400	500	600	400	500	600
	Reaction pressure (atm)	245	360	440	250	345	430	250	340	440
	Catalyst, % 10	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	KOH	KOH	KOH
Carboxylic acids	Glycolic acid	21.16	16.83	11.60	12.13	8.75	4.56	15.23	13.90	8.78
	Formic acid	17.97	13.69	8.96	10.95	13.41	7.86	11.45	11.02	6.84
	Acetic acid	22.38	21.45	11.07	17.45	13.09	6.08	12.34	19.12	4.09
Furfurals	5-Methyl furfural	17.23	13.23	6.53	14.34	11.11	5.87	7.83	7.65	3.74
	5-Hydroxymethyl furfural	6.45	5.14	1.23	5.14	2.79	0.76	3.48	2.32	0.67
	Furfural	20.15	10.56	7.80	9.87	4.32	5.09	10.10	7.15	2.59
Aldehydes and ketones		1.89	0.22	2.41	0.98	0.06	0.00	0.65	0.04	0.01
	3-Methyl-2-cyclopentene-1-one									
	2-Cyclo-pentan-1-one	0.78	0.10	0.06	0.56	0.21	0.11	0.23	0.05	0.15
	Formaldehyde	0.65	0.18	0.14	0.45	0.10	0.09	0.34	0.09	0.10
	Acetaldehyde	3.45	0.52	0.27	0.42	0.33	0.24	0.22	0.65	0.23
	Acetone and propionaldehyde	1.56	1.14	0.12	2.67	0.09	0.45	2.34	1.11	0.33
Phenols	Phenol	2.07	1.02	1.01	1.03	1.01	0.98	0.67	0.45	0.56
	m-& p-cresol	0.88	0.44	0.00	0.34	0.80	0.03	0.45	0.23	0.02
	o-cresol	4.89	0.69	0.36	1.14	2.54	0.83	2.13	0.89	0.02
	Resorcinol	0.34	0.11	1.32	0.16	0.18	0.12	0.38	0.22	0.08
	Catechol	0.48	0.15	0.02	0.22	0.13	0.13	0.42	0.06	0.03
	3-methoxy catechol	0.54	0.00	0.06	0.23	0.06	0.05	0.23	0.00	0.03
	methoxy benzene+4- methoxy phenol	5.67	2.38	1.20	1.56	3.54	2.25	1.34	1.33	0.14
	2-6 Di methoxy phenol	0.35	0.29	0.16	0.22	0.33	0.08	0.12	0.12	0.04
	2- methoxy phenol + 3- methoxy phenol	0.12	0.08	0.03	0.08	0.05	0.05	0.05	0.03	0.02
	4-methyl guaiacol	1.07	1.18	0.01	0.93	1.75	0.03	0.09	1.12	0.01
	3,4 methyl phenol	0.39	0.22	0.10	0.45	0.31	0.52	0.29	0.22	0.02
	4-vinyl guaiacol	0.33	0.07	0.00	0.65	0.38	0.00	0.11	0.00	0.01
	3,5 dimethyl phenol	0.12	0.14	0.00	0.05	0.32	0.00	0.10	0.02	0.00

Table 5.3.12. Concentrations of major organic compounds identified in liquid product from the gasification of tannic acid in relation to catalyst and temperature

Yield (g/kg tannic acid)	Reaction temperature (°C)	400	500	600	400	500	600
	Reaction pressure (atm)	260	340	440	260	340	440
	Catalyst, % 10	AC-Ni	AC-Ni	AC-Ni	AC-Ru	AC-Ru	AC-Ru
Carboxylic acids	Glycolic acid	43.23	36.19	15.65	48.15	42.13	12.56
	Formic acid	24.78	19.45	10.12	21.34	22.78	5.65
	Acetic acid	32.23	25.34	17.18	29.87	21.56	12.45
Furfurals	5-Methyl furfural	26.13	22.13	8.88	20.89	15.65	4.56
	5-Hydroxymethyl furfural	4.43	1.45	2.31	2.15	1.49	1.25
	Furfural	10.99	5.39	8.45	7.15	2.37	3.15
Aldehydes and ketones		1.09	1.25	1.14	1.02	2.15	1.56
	3-Methyl-2-cyclopentene-1-one						
	2-Cyclo-pentan-1-one	0.55	0.56	0.02	0.23	0.08	0.02
	Formaldehyde	0.34	0.42	1.21	0.39	0.49	2.33
	Acetaldehyde	4.88	3.92	2.95	4.87	3.02	1.95
	Acetone and propionaldehyde	5.16	1.44	0.02	4.99	3.45	0.09
Phenols	Phenol	1.78	2.13	1.01	1.79	2.03	1.06
	m- & p-cresol	0.93	0.05	0.00	0.03	1.05	0.07
	o-cresol	4.89	2.19	1.37	3.09	2.38	1.37
	Resorcinol	0.45	0.01	1.12	0.05	0.45	0.05
	Catechol	0.01	0.08	0.01	0.00	0.97	0.05
	3-methoxy catechol	0.02	0.00	0.34	0.00	0.09	0.38
	methoxy benzene+4- methoxy	4.12	3.39	3.21	3.19	3.22	1.05
	Phenol						
	2-6 Di methoxy phenol	0.66	0.34	0.16	0.45	0.34	0.13
	2- methoxy phenol + 3-	0.05	0.09	0.03	0.02	0.04	0.12
	methoxy phenol						
	4-methyl guaiacol	1.03	1.23	0.01	1.09	1.03	0.23
	3,4 methyl phenol	0.32	0.07	0.09	0.39	0.06	0.05
	4-vinyl guaiacol	0.05	0.07	0.04	0.05	0.02	0.00
	3,5 dimethyl phenol	0.19	0.12	0.02	0.00	0.19	0.00
	Total Phenol (colorimetric)	6.25	8.70	9.00	8.50	8.00	7.00

Table 5.3.13 Concentrations of major organic compounds identified in liquid product from the gasification of tannic acid in relation to pressure for the reaction temperature of 400°C.

Yield (g/kg tannic acid)	Reaction pressure	205	280	350	423	200	275	345	419
	Catalyst, % 10	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Carboxylic acids									
	Glycolic acid	11.23	15.78	16.23	10.25	9.78	12.23	18.75	5.45
	Formic acid	14.22	15.12	11.25	6.95	9.78	15.12	17.17	11.12
	Acetic acid	29.33	21.67	16.89	12.11	21.78	12.67	9.87	3.32
Furfurals									
	5-Methyl furfural	24.45	20.34	12.67	10.98	22.21	18.73	11.63	11.76
	5-Hydroxymethyl furfural	7.17	5.67	1.13	1.25	4.78	2.13	1.89	1.45
	Furfural	16.34	19.56	22.88	12.34	4.56	3.45	2.12	1.29
Aldehydes and ketones									
	3-Methyl-2-cyclopentene-1-one	0.65	0.97	0.43	0.32	0.65	0.65	0.65	0.15
	2-Cyclo-pentan-1-one	0.78	0.68	0.67	0.45	0.78	0.78	0.78	0.22
	Formaldehyde	0.65	0.88	0.48	1.05	0.65	0.44	0.33	0.26
	Acetaldehyde	3.45	2.14	1.73	1.89	3.45	1.57	0.87	1.67
	Acetone and propionaldehyde	3.56	1.25	3.00	1.78	3.56	2.44	1.23	1.28
Phenols									
	Phenol	1.89	2.12	2.02	0.97	1.89	1.24	0.97	0.93
	m- & p-cresol	1.23	1.76	1.00	1.45	1.23	1.35	1.02	1.28
	o-cresol	3.12	2.45	2.66	2.34	3.12	1.68	1.98	2.88
	Resorcinol	0.78	0.70	0.34	0.65	0.78	1.02	0.76	0.45
	Catechol	0.92	0.94	0.87	0.66	0.92	0.91	0.99	1.34
	3-methoxy catechol	0.96	0.17	0.75	0.67	0.96	0.57	1.21	0.65
	methoxy benzene+4- methoxy phenol	5.87	3.55	1.67	2.62	5.87		2.45	1.87
	2-6 Di methoxy phenol	0.39	0.09	0.24	0.66	0.39	3.71	0.68	0.77
	2- methoxy phenol + 3- methoxy phenol	2.15	2.05	2.02	1.89	2.15	0.75	1.23	1.15
	4-methyl guaiacol	1.23	1.88	1.09	1.29	1.23	1.66	1.26	0.03
	3,4 methyl phenol	0.88	0.29	0.56	0.89	0.88	0.18	0.66	0.78
	4-vinyl guaiacol	0.45	0.06	0.09	0.22	0.45	0.94	0.22	0.15
	3,5 dimethyl phenol	0.18	0.22	0.11	0.08	0.18	1.02	0.05	0.80
	Total Phenol (colorimetric)	7.20	7.03	6.55	6.58	8.80	6.20	6.00	6.20

Table 5.3.14 Concentrations of major organic compounds identified in liquid product from the gasification of tannic acid in relation to pressure for the reaction temperature of 500°C.

Yield (g/kg tannic acid)	Reaction pressure	205	280	350	423	200	275	345	419
	Catalyst, % 10	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Carboxylic acids									
	Glycolic acid	9.45	12.34	15.25	13.45	10.45	12.89	20.56	21.56
	Formic acid	18.76	12.17	6.78	5.99	19.89	15.12	9.87	7.89
	Acetic acid	27.54	20.77	15.63	4.34	19.33	15.33	15.77	7.87
Furfurals									
	5-Methyl furfural	26.99	12.66	5.76	3.44	30.67	20.45	8.77	2.98
	5-Hydroxymethyl furfural	9.10	4.34	0.97	3.56	6.77	1.98	0.56	1.65
	Furfural	14.56	17.88	25.66	4.67	2.66	1.94	2.77	3.76
Aldehydes and ketones									
	3-Methyl-2-cyclopentene-1-one	0.61	0.73	0.19	0.08	1.41	1.41	0.41	1.09
	2-Cyclo-pentan-1-one	0.54	0.44	0.43	0.21	0.54	0.54	0.54	0.02
	Formaldehyde	0.41	0.64	0.24	0.81	0.41	0.2	0.09	0.02
	Acetaldehyde	3.21	1.9	1.49	1.65	3.21	1.33	0.63	1.43
	Acetone and propionaldehit	3.32	1.01	2.76	1.54	3.32	2.2	0.99	1.04
Phenols									
	Phenol	1.65	1.88	1.78	0.73	1.65	1.99	0.73	2.69
	m-& p-cresol	0.99	1.52	1.76	1.21	0.99	1.11	0.78	1.04
	o-cresol	4.88	2.21	2.42	2.1	2.88	1.44	1.74	2.64
	Resorcinol	0.54	0.46	1.01	0.41	0.54	0.78	0.52	0.21
	Catechol	0.68	0.7	0.63	0.42	1.68	0.67	0.75	1.1
	3-methoxy catechol	0.72	-0.07	0.51	0.43	0.72	0.33	0.97	0.41
	methoxy benzene+4- methoxy phenol	6.63	3.31	1.43	2.38	5.63	3.47	2.21	1.63
	2-6 Di methoxy phenol	0.15	-0.15	0	0.42	0.15	0.51	0.44	0.53
	2- methoxy phenol + 3- methoxy phenol	1.91	1.81	1.78	1.65	1.91	1.42	0.99	0.91
	4-methyl guaiacol	0.99	1.64	0.85	1.05	0.99	-0.06	1.02	0.21
	3,4 methyl phenol	0.64	0.05	0.32	0.65	0.64	0.7	0.42	0.54
	4-vinyl guaiacol	1.21	0.18	0.15	0.02	0.21	0.78	0.02	0.09
	3,5 dimethyl phenol	0.06	0.02	0.13	0.16	0.06	0.43	0.19	0.56
	Total Phenol (colorimetric)	6.25	8.70	9.00	8.50	8.00	7.00	7.50	8.80

Table 5.3.15 Concentrations of major organic compounds identified in liquid product from the gasification of tannic acid in relation to pressure for the reaction temperature of 600°C.

Yield (g/kg tannic acid)	Reaction pressure	205	280	350	423	200	275	345	419
	Catalyst, % 10	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Carboxylic acids									
	Glycolic acid	8.67	15.22	13.67	7.69	8.22	9.67	16.19	2.89
	Formic acid	11.66	12.56	18.69	4.39	7.22	12.56	14.61	8.56
	Acetic acid	26.77	19.11	14.33	9.55	19.22	10.11	7.31	0.76
Furfurals									
	5-Methyl furfural	21.89	17.78	16.11	8.42	19.65	16.17	8.07	9.2
	5-Hydroxymethyl furfural	4.61	3.11	3.43	2.31	2.22	0.43	2.67	5.11
	Furfural	13.78	17.00	20.32	9.78	2.36	3.89	1.44	5.27
Aldehydes and ketones									
	3-Methyl-2-cyclopentene-1-one	0.48	0.80	0.26	0.15	0.48	0.48	0.48	0.02
	2-Cyclo-pentan-1-one	0.61	0.51	0.5	0.28	0.61	0.61	0.61	0.05
	Formaldehyde	0.48	2.71	0.31	0.88	0.48	0.27	0.16	0.09
	Acetaldehyde	3.28	1.97	1.56	1.72	3.28	1.4	0.7	1.5
	Acetone and propionaldehit	3.39	1.08	2.83	1.61	3.39	2.27	1.06	1.11
Phenols									
	Phenol	1.72	1.95	1.85	2.87	1.72	1.45	0.8	0.76
	m- & p-cresol	1.06	1.59	0.83	1.28	1.06	1.18	0.85	1.11
	o-cresol	2.95	2.28	2.49	2.17	2.95	1.51	1.81	2.71
	Resorcinol	0.61	0.53	0.17	0.48	0.61	0.85	0.59	0.28
	Catechol	0.75	0.77	0.75	0.49	0.75	0.74	0.82	1.17
	3-methoxy catechol	0.79	2.33	0.58	0.59	0.79	0.4	1.04	0.48
	methoxy benzene+4- methoxy phenol	5.73	3.38	1.5	2.45	5.76	3.54	2.28	1.7
	2-6 Di methoxy phenol	0.22	0.08	0.07	0.49	0.22	0.58	0.51	0.6
	2- methoxy phenol + 3- methoxy phenol	1.98	1.88	1.85	1.72	1.98	1.49	1.06	0.98
	4-methyl guaiacol	1.06	1.71	0.92	1.12	1.06	0.01	1.09	0.14
	3,4 methyl phenol	0.71	0.12	0.39	0.72	0.71	0.77	0.49	0.61
	4-vinyl guaiacol	0.28	0.11	0.08	0.05	0.28	0.85	0.05	0.02
	3,5 dimethyl phenol	0.01	0.05	0.06	0.09	0.01	0.5	0.12	0.63
	Total Phenol (colorimetric)	6.15	5.30	5.30	4.50	4.00	6.00	6.00	5.20

Table 5.3.16 Concentrations of major organic compounds identified in liquid product from the gasification of gallic acid in relation to catalyst and temperature.

Yield (g/kg gallic acid)	Reaction temperature (°C)	400	500	600	400	500	600	400	500	600
	Reaction pressure (atm)	225	360	420	275	340	440	240	370	440
	Catalyst, % 10	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	KOH	KOH	KOH
Carboxylic acids	Glycolic acid	4.63	2.27	1.79	1.49	1.41	0.07	5.33	2.51	1.51
	Formic acid	11.56	5.27	6.50	2.86	1.64	5.61	4.10	3.79	1.24
	Acetic acid	28.13	26.68	7.25	27.27	13.23	7.00	24.92	17.47	13.97
Furfurals	5-Methyl furfural	17.24	14.86	11.79	9.13	8.85	5.40	14.01	13.50	10.84
	5-Hydroxymethyl furfural	2.60	1.19	0.99	2.25	1.78	0.03	1.40	0.01	0.01
	Furfural	0.59	0.27	0.36	0.10	0.09	0.15	0.12	0.09	0.10
Aldehydes and ketones	3-Methyl-2-cyclopentene-1-one	0.48	0.03	0.02	0.43	0.05	0.00	0.45	0.02	0.01
	2-Cyclo-pentan-1-one	1.48	0.36	0.51	0.40	0.12	0.17	0.22	0.11	0.12
	Formaldehyde	0.20	0.02	0.04	0.01	0.01	0.01	0.02	0.02	0.01
	Acetaldehyde	0.44	0.08	0.42	0.13	0.04	0.07	0.10	0.02	0.04
	Acetone and propionaldehyde	5.03	5.48	4.39	4.34	5.27	3.34	5.91	5.66	4.36
Phenols	Phenol	0.04	0.01	0.01	0.03	0.01	0.01	0.17	0.27	0.00
	m-& p-cresol	0.08	1.03	0.14	0.33	0.09	0.18	0.06	0.04	0.02
	o-cresol	0.50	0.01	0.42	0.00	0.00	0.23	2.69	2.75	0.55
	Resorcinol	0.09	0.04	0.04	0.03	0.00	0.01	0.02	0.00	0.01
	Catechol	1.18	0.12	0.33	0.48	0.03	0.15	0.14	0.06	0.06
	3-methoxy catechol	0.08	0.07	0.05	0.15	0.06	0.07	0.05	0.10	0.05
	methoxy benzene+4- methoxy phenol	1.93	4.76	0.46	2.10	4.20	0.33	2.69	2.62	0.29
	2-6 Di methoxy phenol	0.48	0.52	0.22	0.32	0.13	0.14	0.23	0.12	0.13
	2- methoxy phenol + 3-methoxy phenol	0.20	0.10	0.06	0.17	0.07	0.08	0.11	0.06	0.05
	4-methyl guaiacol	0.49	0.46	0.07	0.24	0.48	0.24	0.60	0.62	0.02
	3,4 methyl phenol	0.09	0.10	0.03	0.01	0.15	0.07	0.15	0.21	0.00
	4-vinyl guaiacol	0.04	0.03	0.00	0.09	0.01	0.02	0.07	0.17	0.00
	3,5 dimethyl phenol	0.08	0.13	0.00	0.24	0.29	0.00	0.25	0.29	0.01

Table 5.3.17 Concentrations of major organic compounds identified in liquid product from the gasification of gallic acid in relation to pressure for the reaction temperature of 400°C.

Yield (g/kg gallic acid)	Reaction pressure	210	280	355	440	205	280	360	430
	Catalyst, % 10	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Carboxylic acids	Glycolic acid	5.29	4.93	1.69	0.84	2.78	2.22	2.53	1.83
	Formic acid	3.79	4.26	4.69	8.31	2.39	3.59	6.97	9.55
	Acetic acid	63.12	27.48	17.63	14.55	47.05	42.42	39.35	33.78
Furfurals	5-Methyl furfural	25.88	24.10	20.70	12.90	29.50	20.55	14.56	14.55
	5-Hydroxymethyl furfural	0.96	0.49	0.28	0.06	0.13	0.11	0.06	0.01
	Furfural	1.00	0.32	0.31	0.19	0.23	0.20	0.09	0.02
Aldehydes and ketones	3-Methyl-2-cyclopentene-1-one								
		0.93	1.40	0.67	0.73	0.60	0.69	0.77	0.51
	2-Cyclo-pentan-1-one	1.56	2.73	1.24	1.44	0.27	0.31	0.30	0.13
	Formaldehyde	0.05	0.06	0.03	0.02	0.04	0.02	0.02	0.01
	Acetaldehyde	0.85	1.05	0.86	1.81	2.14	0.95	1.78	0.66
	Acetone and propionaldehyde	5.04	4.15	5.13	5.18	7.28	8.93	5.44	4.79
Phenols	Phenol	0.53	0.09	0.16	0.01	0.03	0.02	0.01	0.01
	m- & p-cresol	0.65	0.12	0.18	0.89	0.81	1.08	1.23	0.98
	o-cresol	3.46	1.83	0.97	0.12	1.50	0.47	0.84	0.68
	Resorcinol	0.12	0.19	0.06	0.05	0.01	0.03	0.02	0.02
	Catechol	1.20	2.30	3.49	2.08	0.03	0.23	0.25	0.33
	3-methoxy catechol	0.10	0.07	0.03	0.05	0.10	0.09	0.04	0.08
	methoxy benzene+4- methoxy phenol								
		1.92	1.88	1.19	1.41	2.40	1.41	1.88	1.84
	2-6 Di methoxy phenol	0.48	0.39	0.26	0.20	0.20	0.26	0.75	0.10
	2- methoxy phenol + 3- methoxy phenol								
		0.17	0.16	0.04	0.02	0.08	0.13	0.10	0.08
	4-methyl guaiacol	0.24	0.52	0.38	0.17	0.78	0.85	0.81	0.67
	3,4 methyl phenol	0.20	0.37	0.11	0.17	0.25	0.33	0.27	0.28
	4-vinyl guaiacol	0.19	0.21	0.09	0.10	0.11	0.16	0.05	0.04
	3,5 dimethyl phenol	0.14	0.09	0.06	0.03	0.28	0.84	0.17	0.12

Table 5.3.18 Concentrations of major organic compounds identified in liquid product from the gasification of gallic acid in relation to pressure for the reaction temperature of 500°C.

Yield (g/kg gallic acid)	Reaction pressure	215	275	360	425	210	280	350	435
	Catalyst, % 10	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Carboxylic acids	Glycolic acid	4.92	2.97	2.93	1.32	2.30	1.28	1.15	2.92
	Formic acid	2.99	3.31	5.74	7.64	2.51	4.37	4.85	9.90
	Acetic acid	35.76	33.47	31.03	25.82	29.24	25.27	16.62	8.74
Furfurals	5-Methyl furfural	23.06	17.24	14.24	10.04	15.25	6.17	5.81	4.78
	5-Hydroxymethyl furfural	1.27	0.49	0.33	0.12	0.15	0.10	0.10	0.09
	Furfural	0.54	1.02	0.76	0.21	0.18	0.36	0.21	0.13
Aldehydes and ketones	3-Methyl-2-cyclopentene-1-one	0.03	0.01	0.00	1.58	0.06	0.09	0.05	0.04
	2-Cyclo-pentan-1-one	0.42	0.52	0.54	0.05	0.10	0.32	0.12	0.11
	Formaldehyde	0.06	0.08	0.07	0.08	0.05	0.87	0.11	0.02
	Acetaldehyde	0.18	0.08	0.11	0.04	0.13	0.33	0.04	0.11
	Acetone and propionaldehit	5.07	4.76	4.86	3.04	3.33	4.67	5.56	4.51
Phenols	Phenol	0.03	0.12	0.08	0.01	0.03	0.06	0.03	0.02
	m- & p-cresol	0.38	0.43	0.56	0.58	0.27	0.43	0.88	1.13
	o-cresol	0.08	0.53	0.16	2.16	0.20	1.31	0.30	0.39
	Resorcinol	0.05	0.13	0.07	0.03	0.01	0.05	0.00	0.01
	Catechol	0.05	0.09	0.09	0.02	0.05	0.11	0.02	0.07
	3-methoxy catechol	0.06	0.08	0.04	0.05	0.27	0.03	0.03	0.05
	methoxy benzene+4- methoxy phenol	3.13	4.71	5.84	2.08	1.53	2.57	4.14	4.52
	2-6 Di methoxy phenol	0.11	0.27	0.22	0.12	0.18	0.15	0.23	0.13
	2- methoxy phenol + 3- methoxy phenol	0.18	0.10	0.15	0.06	0.07	0.06	0.04	0.03
	4-methyl guaiacol	0.16	0.50	0.94	0.90	0.29	0.02	0.70	0.34
	3,4 methyl phenol	0.05	0.05	0.18	0.11	0.00	0.08	0.13	0.11
	4-vinyl guaiacol	0.03	0.04	0.09	0.06	0.07	0.18	0.21	0.18
	3,5 dimethyl phenol	0.10	0.06	0.19	0.22	0.03	0.24	0.30	0.21

Table 5.3.19 Concentrations of major organic compounds identified in liquid product from the gasification of gallic acid in relation to pressure for the reaction temperature of 600°C.

Yield (g/kg gallic acid)	Reaction pressure	210	285	360	430	205	280	355	440
	Catalyst, % 10	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Carboxylic acids									
	Glycolic acid	3.05	2.33	1.79	0.05	3.73	2.20	2.35	2.19
	Formic acid	3.87	4.45	6.05	7.54	8.40	10.51	14.58	17.57
	Acetic acid	38.56	39.09	34.82	13.95	36.32	20.65	13.02	10.86
Furfurals									
	5-Methyl furfural	28.47	23.49	12.61	19.92	16.68	16.00	7.81	7.99
	5-Hydroxymethyl furfural	1.37	0.75	0.06	0.05	0.16	0.13	0.11	0.10
	Furfural	1.47	1.09	0.82	0.11	0.18	0.21	0.23	0.13
Aldehydes and ketones									
	3-Methyl-2-cyclopentene-1-one	0.02	0.00	0.00	0.00	0.04	0.06	0.00	0.01
	2-Cyclo-pentan-1-one	7.30	0.30	0.69	0.01	0.19	0.20	0.12	0.06
	Formaldehyde	0.13	0.12	0.07	0.01	0.05	0.05	0.11	0.04
	Acetaldehyde	0.16	0.14	0.03	0.02	0.17	0.19	0.14	0.10
	Acetone and propionaldehit	2.31	2.15	1.57	1.57	1.97	0.72	0.72	0.48
Phenols									
	Phenol	0.24	0.12	0.08	0.00	0.01	0.03	0.03	0.00
	m- & p-cresol	0.12	0.02	0.00	0.01	0.00	0.04	0.06	0.01
	o-cresol	0.56	0.16	0.00	0.01	0.00	0.07	0.19	0.00
	Resorcinol	0.33	0.01	0.01	0.01	0.01	0.01	0.00	0.01
	Catechol	3.19	0.03	0.04	0.01	0.17	0.04	0.08	0.04
	3-methoxy catechol	0.29	0.02	0.00	0.06	0.09	0.05	0.03	0.03
	methoxy benzene+4- methoxy phenol	3.63	2.15	2.24	2.03	0.25	0.33	1.43	0.48
	2-6 Di methoxy phenol	0.18	0.15	0.12	0.24	0.02	0.15	0.11	0.16
	2- methoxy phenol + 3-methoxy phenol	0.15	0.04	0.11	0.03	0.02	0.08	0.04	0.02
	4-methyl guaiacol	0.72	0.01	0.01	0.01	0.01	0.01	0.01	0.01
	3,4 methyl phenol	0.62	0.00	0.00	0.01	0.00	0.02	0.01	0.00
	4-vinyl guaiacol	0.13	0.00	0.01	0.01	0.00	0.00	0.28	0.00
	3,5 dimethyl phenol	0.00	0.00	0.00	0.00	0.01	0.00	0.40	0.00

Table 5.3.20 Concentrations of major organic compounds identified in liquid product from the gasification of phloroglucinol in relation to catalyst and temperature.

Yield (g /kg phloroglucinol)	Reaction temperature (°C)	400	500	600	400	500	600	400	500	600
Carboxylic acids	Reaction pressure (atm)	240	360	410	220	340	470	215	365	460
	Catalyst, % 10	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	KOH	KOH	KOH
	Glycolic acid	16.06	11.73	6.5	7.03	3.65	0.54	10.13	8.8	3.68
	Formic acid	13.57	9.29	4.56	6.55	9.01	3.46	7.05	6.62	2.44
	Acetic acid	19.08	18.15	7.77	14.15	9.79	2.78	9.04	15.82	0.79
Furfurals	5-Methyl furfural	12.13	8.13	1.43	9.24	6.01	0.77	2.73	2.55	1.30
	5-Hydroxymethyl furfural	2.05	0.74	3.17	0.74	-1.61	3.60	2.02	2.00	3.70
	Furfural	16.85	7.26	4.50	6.57	1.02	1.79	6.80	3.85	2.71
Aldehydes and ketones	3-Methyl-2-cyclopentene-1-one	1.49	0.18	2.01	0.58	0.34	0.4	0.25	0.36	0.39
	2-Cyclo-pentan-1-one	0.58	0.1	0.14	0.36	0.01	0.09	0.03	0.15	0.05
	Formaldehyde	0.45	0.02	0.06	0.25	0.1	0.11	0.14	0.11	0.1
	Acetaldehyde	3.25	0.32	0.07	0.22	0.13	0.04	0.02	0.45	0.03
	Acetone and propionaldehyde	1.36	0.94	0.08	2.47	0.11	0.25	2.14	0.91	0.13
	Phenols	Phenol	1.87	0.82	0.81	0.83	0.81	0.78	0.47	0.25
m-& p-cresol		0.68	0.24	0.2	0.14	0.6	0.17	0.25	0.03	0.18
o-cresol		4.69	0.49	0.16	0.94	2.34	0.63	1.93	0.69	0.18
Resorcinol		0.14	0.09	1.12	0.04	0.02	0.08	0.18	0.02	0.12
Catechol		0.28	0.05	0.18	0.02	0.07	0.07	0.22	0.14	0.17
3-methoxy catechol		0.34	0.2	0.14	0.03	0.14	0.15	0.03	-0.2	0.17
methoxy benzene+4- methoxy phenol		5.47	2.18	1.00	1.36	3.34	2.05	1.14	1.13	0.06
2-6 Di methoxy phenol		0.15	0.09	0.04	0.02	0.13	0.12	0.08	0.08	0.16
2- methoxy phenol + 3- methoxy phenol		0.08	0.12	0.17	0.12	0.15	0.15	0.3	0.17	0.18
4-methyl guaiacol		0.87	0.98	0.19	0.73	1.55	0.17	0.11	0.92	0.19
3,4 methyl phenol		0.19	0.02	0.1	0.25	0.11	0.32	0.09	0.02	0.18
4-vinyl guaiacol		0.13	0.13	0.2	0.45	0.18	0.2	0.09	0.2	0.19
3,5 dimethyl phenol		0.08	0.06	0.2	0.15	0.12	0.2	0.10	0.0	0.2

Table 5.3.21 Concentrations of major organic compounds identified in liquid product from the gasification of phloroglucinol in relation to pressure for the reaction temperature of 400°C.

Yield (g /kg phloroglucinol)	Reaction pressure	200	270	355	420	200	270	345	420
	Catalyst, % 10	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Carboxylic acids									
	Glycolic acid	12.09	11.60	9.13	2.32	6.94	5.75	10.19	5.33
	Formic acid	19.10	19.18	7.59	0.10	11.13	15.52	14.01	6.37
	Acetic acid	91.95	67.54	45.12	12.80	64.68	110.31	90.75	78.33
Furfurals									
	5-Methyl furfural	37.03	50.50	19.05	7.39	34.82	89.65	56.02	45.19
	5-Hydroxymethyl furfural	91.27	34.39	22.83	74.16	11.72	118.12	27.86	36.45
	Furfural	27.76	27.91	12.80	0.91	1.17	2.07	2.30	0.15
Aldehydes and ketones									
	3-Methyl-2-cyclopentene-1-one	1.84	2.07	2.47	0.77	1.05	1.31	1.21	0.58
	2-Cyclo-pentan-1-one	1.19	2.26	3.93	3.12	0.41	0.55	0.44	0.31
	Formaldehyde	0.49	0.26	0.18	0.05	0.17	0.05	0.05	0.05
	Acetaldehyde	4.47	2.93	4.14	3.27	2.22	2.63	1.89	1.42
	Acetone and propionaldehyde	10.35	5.55	0.62	1.34	9.14	2.96	1.49	2.94
Phenols									
	Phenol	0.05	0.07	0.04	0.30	0.02	0.01	0.02	0.00
	m-& p-cresol	0.53	0.38	0.56	0.28	1.28	0.65	2.46	2.20
	o-cresol	2.00	0.07	1.46	0.19	1.87	0.23	1.41	0.01
	Resorcinol	1.43	1.52	0.82	0.05	0.05	0.09	0.07	0.01
	Catechol	1.54	1.80	2.78	2.07	0.19	0.41	0.56	0.88
	3-methoxy catechol	0.30	0.06	0.06	0.01	0.08	0.15	0.10	0.14
	methoxy benzene+4- methoxy phenol	2.58	2.01	1.03	1.19	3.90	2.38	1.59	2.83
	2-6 Di methoxy phenol	0.56	0.36	0.28	0.28	0.32	0.41	0.39	0.23
	2- methoxy phenol + 3- methoxy phenol	0.20	0.16	0.06	0.04	0.16	0.07	0.10	0.02
	4-methyl guaiacol	0.85	0.47	0.48	0.30	1.60	1.56	1.36	0.85
	3,4 methyl phenol	0.28	0.53	0.10	0.23	0.60	0.97	0.58	0.35
	4-vinyl guaiacol	0.01	0.01	0.02	0.04	0.35	0.10	0.01	0.03
	3,5 dimethyl phenol	0.03	0.32	0.15	0.15	0.17	0.36	0.26	0.17
	Total Phenol (colorimetric)								

Table 5.3.22 Concentrations of major organic compounds identified in liquid product from the gasification of phloroglucinol in relation to pressure for the reaction temperature of 500°C.

Yield (g/kg phloroglucinol)	Reaction pressure	195	270	350	420	202	275	355	430
	Catalyst, % 10	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Carboxylic acids	Glycolic acid	10.12	5.46	14.40	4.87	6.59	0.39	2.19	9.57
	Formic acid	13.58	9.62	20.34	3.81	7.80	14.47	6.05	19.03
	Acetic acid	36.50	49.28	48.46	5.08	50.94	21.51	23.97	32.96
Furfurals	5-Methyl furfural	50.22	18.73	31.76	3.82	21.40	11.55	22.58	24.08
	5-Hydroxymethyl furfural	17.99	16.43	18.16	12.36	5.62	10.20	14.40	15.30
	Furfural	37.41	9.68	11.68	4.88	2.92	1.99	2.74	1.66
Aldehydes and ketones	3-Methyl-2-cyclopentene-1-one	0.04	0.02	0.01	0.05	0.06	0.16	0.16	0.01
	2-Cyclo-pentan-1-one	0.21	0.10	0.07	0.07	0.14	0.14	0.11	0.05
	Formaldehyde	0.62	0.55	0.46	0.55	0.06	1.10	1.58	1.07
	Acetaldehyde	2.59	0.60	0.31	0.99	0.37	0.31	1.88	0.39
	Acetone and propionaldehit	2.76	1.34	9.38	2.16	0.56	2.30	1.32	1.41
Phenols	Phenol	1.56	0.14	0.35	0.27	0.11	0.07	0.05	0.02
	m- & p-cresol	0.09	0.00	0.22	0.14	0.14	2.01	1.67	1.21
	o-cresol	0.02	0.00	0.02	0.05	0.18	1.85	1.88	0.13
	Resorcinol	2.30	3.26	2.62	6.68	2.72	2.84	3.12	2.92
	Catechol	0.13	0.05	0.09	0.15	0.07	0.14	0.08	0.05
	3-methoxy catechol	0.02	0.02	0.05	0.02	0.03	0.03	0.01	0.01
	methoxy benzene+4- methoxy phenol	3.44	2.61	3.63	3.74	2.21	3.37	3.06	2.65
	2-6 Di methoxy phenol	0.10	0.01	0.16	0.11	0.13	0.38	0.19	0.16
	2- methoxy phenol + 3- methoxy phenol	0.05	0.01	0.02	0.01	0.02	0.02	0.00	0.01
	4-methyl guaiacol	0.67	0.84	0.76	0.15	0.53	1.02	0.88	0.00
	3,4 methyl phenol	0.66	0.20	0.27	0.03	0.38	0.65	0.37	0.32
	4-vinyl guaiacol	0.59	0.06	0.35	0.10	0.30	0.56	0.45	0.62
	3,5 dimethyl phenol	4.30	1.94	2.26	1.55	1.22	2.84	0.38	0.68
	Total Phenol (colorimetric)								

Table 5.3.23 Concentrations of major organic compounds identified in liquid product from the gasification of phloroglucinol in relation to pressure for the reaction temperature of 600°C.

Yield (g/kg phloroglucinol)	Reaction pressure	205	280	350	420	201	280	350	425
	Catalyst, % 10	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Carboxylic acids									
	Glycolic acid	20.22	12.24	20.87	7.64	5.86	2.85	4.28	0.78
	Formic acid	18.17	14.91	18.95	5.45	7.49	10.10	11.37	19.08
	Acetic acid	97.41	66.87	69.26	11.53	66.06	30.80	39.18	44.39
Furfurals									
	5-Methyl furfural	56.01	36.02	37.92	9.57	36.45	23.79	19.73	20.61
	5-Hydroxymethyl furfural	33.62	13.33	0.51	5.52	2.69	1.40	3.97	3.86
	Furfural	32.06	18.91	29.93	10.57	2.72	0.70	0.93	2.03
Aldehydes and ketones									
	3-Methyl-2-cyclopentene-1-one	0.10	0.02	0.08	0.03	0.10	0.02	0.07	0.01
	2-Cyclo-pentan-1-one	0.16	0.05	0.09	0.02	0.38	0.01	0.02	0.05
	Formaldehyde	0.44	0.17	0.45	0.11	0.76	0.05	0.13	0.14
	Acetaldehyde	0.56	0.32	0.18	0.40	0.22	0.03	0.34	0.42
	Acetone and propionaldehit	3.05	1.61	1.74	2.58	0.45	0.07	0.29	0.39
Phenols									
	Phenol	0.74	0.43	1.17	0.34	0.07	0.01	0.01	0.04
	m- & p-cresol	0.25	0.04	0.01	0.01	0.13	0.05	0.22	0.04
	o-cresol	0.06	0.08	0.03	0.01	0.07	0.02	0.07	0.05
	Resorcinol	2.02	1.84	1.12	1.13	0.08	0.15	0.21	0.45
	Catechol	0.06	0.01	0.11	0.00	0.05	0.01	0.11	0.03
	3-methoxy catechol	0.02	0.02	0.10	0.02	0.01	0.01	0.05	0.04
	methoxy benzene+4- methoxy phenol	1.76	1.53	2.11	1.94	0.21	0.08	0.59	0.28
	2-6 Di methoxy phenol	0.04	0.03	0.00	0.19	0.03	0.00	0.04	0.09
	2- methoxy phenol + 3- methoxy phenol	0.03	0.03	0.02	0.01	0.00	0.00	0.00	0.00
	4-methyl guaiacol	0.01	0.01	0.01	0.00	0.00	0.12	0.01	0.01
	3,4 methyl phenol	0.27	0.11	0.44	0.08	0.02	0.09	0.02	0.07
	4-vinyl guaiacol	0.79	0.19	1.34	0.09	0.05	0.09	0.24	0.08
	3,5 dimethyl phenol	0.08	1.84	3.49	1.54	0.54	0.27	0.29	0.15

Table 5.3.24 Concentrations of major organic compounds identified in liquid product from the gasification of pyrogallol in relation to catalyst and temperature.

Yield (g/kg pyrogallol)	Reaction temperature (°C)	400	500	600	400	500	600	400	500	600
	Reaction pressure (atm) Catalyst, % 10	245	360	420	240	350	425	220	360	450
Carboxylic acids	Glycolic acid	17.56	13.23	10.00	8.53	5.15	0.96	11.63	10.30	17.56
	Formic acid	15.47	11.19	8.00	8.45	10.91	5.36	8.95	8.52	15.47
	Acetic acid	17.38	14.00	6.07	12.45	8.09	1.08	7.34	14.12	17.38
Furfurals	5-Methyl furfural	12.03	9.00	1.33	9.14	5.91	0.67	2.63	2.45	12.03
	5-Hydroxymethyl furfural	5.05	3.74	1.03	4.94	2.59	0.56	3.28	2.12	5.05
	Furfural	17.15	7.56	4.80	6.87	2.40	3.20	5.40	4.00	17.15
Aldehydes and ketones	3-Methyl-2-cyclopentene-1-one	2.09	0.42	2.61	1.18	0.26	0.20	0.85	0.24	2.09
	2-Cyclo-pentan-1-one	0.50	0.20	0.16	0.66	0.31	0.21	0.33	0.15	0.50
	Formaldehyde	0.30	0.28	0.24	0.55	0.20	0.19	0.44	0.19	0.30
	Acetaldehyde	2.40	0.62	0.37	0.52	0.43	0.34	0.32	0.75	2.40
	Acetone and propionaldehyde	1.00	1.24	0.22	2.77	0.19	0.55	2.44	1.21	1.00
Phenols	Phenol	1.36	0.94	0.32	2.47	0.29	0.25	2.14	0.91	1.36
	m-& p-cresol	1.87	0.82	0.81	1.13	1.21	0.78	0.47	0.25	1.87
	o-cresol	0.68	0.24	-0.20	0.14	0.60	0.20	0.25	0.03	0.68
	Resorcinol	4.69	0.49	0.16	0.94	2.34	0.63	1.93	0.69	4.69
	Catechol	0.14	0.31	1.52	0.36	0.38	0.32	0.58	0.02	0.14
	3-methoxy catechol	0.28	0.35	0.22	0.42	0.33	0.33	0.62	0.26	0.28
	methoxy benzene+4- methoxy phenol	0.34	0.20	0.26	0.43	0.26	0.25	0.43	0.20	0.34
	2-6 Di methoxy phenol	5.47	2.58	1.40	1.76	3.74	2.45	1.54	1.53	5.47
	2- methoxy phenol + 3-methoxy phenol	0.15	0.49	0.36	0.42	0.53	0.28	0.32	0.32	0.15
	4-methyl guaiacol	0.10	0.28	0.23	0.28	0.25	0.25	0.70	0.23	0.10
	3,4 methyl phenol	0.87	1.38	0.21	1.13	1.95	0.23	0.29	1.32	0.87
	4-vinyl guaiacol	0.19	0.42	0.30	0.65	0.51	0.72	0.49	0.42	0.19
	3,5 dimethyl phenol	0.13	0.27	0.20	0.85	0.58	0.20	0.31	0.20	0.13

Table 5.3.25 Concentrations of major organic compounds identified in liquid product from the gasification of pyrogallol in relation to pressure for the reaction temperature of 400°C.

Yield (g/kg pyrogallol)	Reaction pressure	195	270	345	420	205	270	345	425
	Catalyst, % 10	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Carboxylic acids	Glycolic acid	8.26	10.36	8.96	5.55	6.28	7.23	10.64	3.64
	Formic acid	9.01	9.69	7.97	7.63	6.09	9.36	12.07	10.34
	Acetic acid	46.23	24.58	17.26	13.33	34.42	27.55	24.61	18.55
Furfurals	5-Methyl furfural	25.17	22.22	16.69	11.94	25.86	19.64	13.10	13.16
	5-Hydroxymethyl furfural	4.07	3.08	0.71	0.66	2.46	1.12	0.98	0.73
	Furfural	8.67	9.94	11.60	6.27	2.40	1.83	1.11	0.66
Aldehydes and ketones	3-Methyl-2-cyclopentene-1-one								
		0.79	1.19	0.55	0.53	0.63	0.67	0.71	0.33
	2-Cyclo-pentan-1-one	1.17	1.71	0.96	0.95	0.53	0.55	0.54	0.18
	Formaldehyde	0.35	0.47	0.26	0.54	0.35	0.23	0.18	0.14
	Acetaldehyde	2.15	1.60	1.30	1.85	2.80	1.26	1.33	1.17
	Acetone and propionaldehyde	4.30	2.70	4.07	3.48	5.42	5.69	3.34	3.04
Phenols	Phenol	1.21	1.11	1.09	0.49	0.96	0.63	0.49	0.47
	m-& p-cresol	0.94	0.94	0.59	1.17	1.02	1.22	1.13	1.13
	o-cresol	3.29	2.14	1.82	1.23	2.31	1.08	1.41	1.78
	Resorcinol	0.45	0.45	0.20	0.35	0.40	0.53	0.39	0.24
	Catechol	1.06	1.62	2.18	1.37	0.48	0.57	0.62	0.84
	3-methoxy catechol	0.53	0.12	0.39	0.36	0.53	0.33	0.63	0.37
	methoxy benzene+4- methoxy phenol								
		3.90	2.72	1.43	2.02	4.14	2.56	2.17	1.86
	2-6 Di methoxy phenol	0.44	0.24	0.25	0.43	0.30	0.51	0.72	0.44
	2- methoxy phenol + 3- methoxy phenol								
		1.16	1.11	1.03	0.96	1.12	0.90	0.67	0.62
	4-methyl guaiacol	0.74	1.20	0.74	0.73	1.01	0.52	1.04	0.35
	3,4 methyl phenol	0.54	0.33	0.34	0.53	0.57	0.64	0.47	0.53
	4-vinyl guaiacol	0.32	0.14	0.09	0.16	0.28	0.59	0.14	0.10
	3,5 dimethyl phenol	0.16	0.16	0.09	0.06	0.23	0.76	0.11	0.46
	Total Phenol (colorimetric)	3.60	3.52	3.28	3.29	4.40	3.10	3.00	3.10

Table 5.3.26 Concentrations of major organic compounds identified in liquid product from the gasification of pyrogallol in relation to pressure for the reaction temperature of 500°C.

Yield (g/kg pyrogallol)	Reaction pressure Catalyst, % 10	229	230	231	232	233	234	235	236
		-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Carboxylic acids									
	Glycolic acid	7.19	10.66	9.09	7.39	6.38	7.09	10.86	12.24
	Formic acid	10.88	9.74	6.26	6.82	11.20	9.75	7.36	8.90
	Acetic acid	31.65	27.12	23.33	15.08	24.29	20.30	16.20	8.31
Furfurals									
	5-Methyl furfural	25.03	14.95	10.00	6.74	22.96	13.31	7.29	3.88
	5-Hydroxymethyl furfural	5.19	2.42	0.65	1.84	3.46	1.04	0.33	0.87
	Furfural	7.55	9.45	13.21	2.44	1.42	1.15	1.49	1.95
Aldehydes and ketones									
	3-Methyl-2-cyclopentene-1-one	0.32	0.37	0.10	0.83	0.74	0.75	0.23	0.57
	2-Cyclo-pentan-1-one	0.48	0.48	0.49	0.13	0.32	0.43	0.33	0.07
	Formaldehyde	0.24	0.36	0.16	0.45	0.23	0.54	0.10	0.02
	Acetaldehyde	1.70	0.99	0.80	0.85	1.67	0.83	0.34	0.77
	Acetone and propionaldehit	4.20	2.89	3.81	2.29	3.33	3.44	3.28	2.78
Phenols									
	Phenol	0.84	1.00	0.93	0.37	0.84	1.03	0.38	1.36
	m- & p-cresol	0.69	0.98	1.16	0.90	0.63	0.77	0.83	1.09
	o-cresol	2.48	1.37	1.29	2.13	1.54	1.38	1.02	1.52
	Resorcinol	0.30	0.30	0.54	0.22	0.28	0.42	0.26	0.11
	Catechol	0.37	0.40	0.36	0.22	0.87	0.39	0.39	0.59
	3-methoxy catechol	0.39	0.01	0.28	0.24	0.50	0.18	0.50	0.23
	methoxy benzene+4- methoxy phenol	4.88	4.01	3.64	2.23	3.58	3.02	3.18	3.08
	2-6 Di methoxy phenol	0.13	0.06	0.11	0.27	0.17	0.33	0.34	0.33
	2- methoxy phenol + 3- methoxy phenol	1.05	0.96	0.97	0.86	0.99	0.74	0.52	0.47
	4-methyl guaiacol	0.58	1.07	0.90	0.98	0.64	-0.02	0.86	0.28
	3,4 methyl phenol	0.35	0.05	0.25	0.38	0.32	0.39	0.28	0.33
	4-vinyl guaiacol	0.62	0.11	0.12	0.04	0.14	0.48	0.12	0.14
	3,5 dimethyl phenol	0.08	0.04	0.16	0.19	0.05	0.34	0.25	0.39

Table 5.3.27 Concentrations of major organic compounds identified in liquid product from the gasification of pyrogallol in relation to pressure for the reaction temperature of 600°C.

Yield (g/kg)	Reaction pressure	237	238	239	240	241	242	243	244
	Catalyst, % 10	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Carboxylic acids	Glycolic acid	5.86	8.78	7.73	3.87	5.98	5.94	9.27	2.54
	Formic acid	7.77	8.51	12.37	5.97	7.81	11.54	14.60	13.07
	Acetic acid	32.67	29.10	24.58	11.75	27.77	15.38	10.17	5.81
Furfurals	5-Methyl furfural	25.18	20.64	14.36	14.17	18.17	16.09	7.94	8.60
	5-Hydroxymethyl furfural	2.99	1.93	1.75	1.18	1.19	0.28	1.39	2.61
	Furfural	7.63	9.05	10.57	4.95	1.27	2.05	0.84	2.70
Aldehydes and ketones	3-Methyl-2-cyclopentene-1-one	0.25	0.40	0.13	0.08	0.26	0.27	0.24	0.02
	2-Cyclo-pentan-1-one	3.96	0.41	0.60	0.15	0.40	0.41	0.37	0.06
	Formaldehyde	0.31	1.42	0.19	0.45	0.27	0.16	0.14	0.07
	Acetaldehyde	1.72	1.06	0.80	0.87	1.73	0.80	0.42	0.80
	Acetone and propionaldehit	2.85	1.62	2.20	1.59	2.68	1.50	0.89	0.80
Phenols	Phenol	0.98	1.04	0.97	1.44	0.87	0.74	0.42	0.38
	m- & p-cresol	0.59	0.81	0.42	0.65	0.53	0.61	0.46	0.56
	o-cresol	1.76	1.22	1.25	1.09	1.48	0.79	1.00	1.36
	Resorcinol	0.47	0.27	0.09	0.25	0.31	0.43	0.30	0.15
	Catechol	1.97	0.40	0.40	0.25	0.46	0.39	0.45	0.61
	3-methoxy catechol	0.54	1.18	0.29	0.33	0.44	0.23	0.54	0.26
	methoxy benzene+4- methoxy phenol	4.68	2.77	1.87	2.24	3.01	1.94	1.86	1.09
	2-6 Di methoxy phenol	0.20	0.12	0.10	0.37	0.12	0.37	0.31	0.38
	2- methoxy phenol + 3- methoxy phenol	1.07	0.96	0.98	0.88	1.00	0.79	0.55	0.50
	4-methyl guaiacol	0.89	0.86	0.47	0.57	0.54	0.01	0.55	0.08
	3,4 methyl phenol	0.67	0.06	0.20	0.37	0.36	0.40	0.25	0.31
	4-vinyl guaiacol	0.21	0.06	0.05	0.03	0.14	0.43	0.17	0.01
	3,5 dimethyl phenol	0.01	0.03	0.03	0.05	0.01	0.25	0.26	0.32

Table 5.3.28 Concentrations of major organic compounds identified in liquid product from the gasification of pectin in relation to catalyst and temperature.

Yield (g/kg pectin)	Reaction temperature (°C)	400	500	600	400	500	600	400	500	600
	Reaction pressure (atm)	235	350	425	230	340	430	225	355	460
	Catalyst, % 10	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	KOH	KOH	KOH
Carboxylic acids	Glycolic acid	6.46	2.25	1.91	0.84	0.85	0.04	2.75	1.71	0.90
	Formic acid	17.23	21.41	9.13	1.99	3.46	7.10	2.77	4.99	8.48
	Acetic acid	33.80	23.70	9.43	23.89	11.89	9.06	20.85	19.81	14.83
Furfurals	5-Methyl furfural	34.54	19.67	26.53	34.98	15.44	6.91	37.72	22.25	17.90
	5-Hydroxymethyl furfural	2.52	1.64	0.52	2.45	2.03	0.04	0.73	0.01	0.01
	Furfural	0.49	0.23	0.39	0.05	0.08	0.15	0.09	0.09	0.07
Aldehydes and ketones	3-Methyl-2-cyclopentene-1-one	0.27	0.02	0.02	0.26	0.03	0.00	0.25	0.01	0.01
	2-Cyclo-pentan-1-one	0.94	0.22	0.58	0.23	0.08	0.18	0.16	0.08	0.06
	Formaldehyde	0.11	0.02	0.05	0.01	0.01	0.01	0.02	0.02	0.01
	Acetaldehyde	0.45	0.10	0.58	0.11	0.06	0.10	0.06	0.02	0.05
	Acetone and propionaldehyde	5.11	2.74	2.20	2.17	3.04	2.84	2.96	2.83	2.25
Phenols	Phenol							0.09	0.14	0.00
	m-& p-cresol	0.25	0.01	0.63	0.00	0.00	0.35	0.09	0.06	0.03
	o-cresol	0.08	0.04	0.05	0.02	0.00	0.01	1.35	1.45	0.28
	Resorcinol	0.98	0.09	0.48	0.29	0.04	0.19	0.02	0.00	0.01
	Catechol	0.07	0.06	0.04	0.09	0.04	0.04	0.09	0.04	0.06
	3-methoxy catechol	1.93	4.76	0.59	2.13	4.64	0.33	0.03	0.07	0.03
	methoxy benzene+4- methoxy phenol	0.63	0.42	0.33	0.32	0.14	0.17	2.76	3.66	0.28
	2-6 Di methoxy phenol	0.26	0.11	0.09	0.16	0.05	0.08	0.22	0.13	0.14
	2- methoxy phenol + 3-methoxy phenol	0.37	0.40	0.04	0.34	0.33	0.13	0.11	0.05	0.07
	4-methyl guaiacol	0.10	0.05	0.02	0.01	0.16	0.04	0.42	0.39	0.03
	3,4 methyl phenol	0.06	0.04	0.00	0.14	0.01	0.03	0.09	0.20	0.00
	4-vinyl guaiacol	0.12	0.20	0.00	0.36	0.44	0.00	0.11	0.25	0.00
	3,5 dimethyl phenol	0.10	0.20	0.03	0.03	0.02	0.01	0.38	0.44	0.01

Table 5.3.29 Concentrations of major organic compounds identified in liquid product from the gasification of pectin in relation to pressure for the reaction temperature of 400°C.

Yield (g/kg pectin)	Reaction pressure	210	280	355	440	205	280	360	430
	Catalyst, % 10	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Carboxylic acids	Glycolic acid	2.73	2.58	0.85	0.70	1.42	1.15	2.64	0.97
	Formic acid	3.80	2.80	2.42	5.41	1.51	2.47	5.50	8.44
	Acetic acid	21.02	18.61	14.98	12.25	31.06	28.82	25.93	23.82
Furfurals	5-Methyl furfural	12.94	31.79	21.72	17.31	44.18	38.03	31.84	31.68
	5-Hydroxymethyl furfural	1.03	0.52	0.30	0.07	0.14	0.12	0.07	0.01
	Furfural	0.73	0.44	0.34	0.23	0.20	0.12	0.06	0.03
Aldehydes and ketones	3-Methyl-2-cyclopentene-1-one	0.63	0.71	0.40	0.37	0.33	0.39	0.46	0.28
	2-Cyclo-pentan-1-one	0.86	1.59	1.21	1.30	0.15	0.23	0.22	0.10
	Formaldehyde	0.03	0.03	0.02	0.01	0.02	0.01	0.02	0.01
	Acetaldehyde	0.46	0.79	0.74	1.38	1.14	0.51	1.27	0.34
	Acetone and propionaldehyde	2.81	4.19	4.45	3.84	4.76	6.05	4.38	3.99
Phenols	Phenol	0.27	0.05	0.09	0.01	0.02	0.02	0.01	0.01
	m- & p-cresol	0.39	0.06	0.27	1.28	0.64	0.85	1.01	0.74
	o-cresol	1.84	0.92	0.57	0.06	1.61	0.24	0.52	0.41
	Resorcinol	0.09	0.22	0.08	0.05	0.01	0.02	0.01	0.01
	Catechol	0.85	2.24	4.77	2.31	0.02	0.15	0.15	0.23
	3-methoxy catechol	0.12	0.06	0.04	0.03	0.06	0.06	0.02	0.04
	methoxy benzene+4- methoxy phenol	2.05	1.98	1.57	1.67	2.34	1.51	1.82	1.79
	2-6 Di methoxy phenol	0.64	0.54	0.38	0.29	0.12	0.25	0.39	0.07
	2- methoxy phenol + 3- methoxy phenol	0.22	0.21	0.06	0.03	0.08	0.14	0.06	0.06
	4-methyl guaiacol	0.20	0.57	0.49	0.14	0.52	0.58	0.43	0.36
	3,4 methyl phenol	0.11	0.34	0.12	0.15	0.21	0.17	0.16	0.16
	4-vinyl guaiacol	0.23	0.27	0.14	0.14	0.17	0.14	0.08	0.06
	3,5 dimethyl phenol	0.21	0.13	0.07	0.04	0.42	0.63	0.25	0.18

Table 5.3.30 Concentrations of major organic compounds identified in liquid product from the gasification of pectin in relation to pressure for the reaction temperature of 500°C.

Yield (g/kg pectin)	Reaction pressure	215	275	360	425	210	280	350	435
	Catalyst, % 10	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Carboxylic acids	Glycolic acid	2.52	1.58	1.48	0.67	1.17	0.64	0.60	1.46
	Formic acid	2.46	2.34	3.34	4.08	2.57	3.44	3.67	12.45
	Acetic acid	26.43	20.25	21.06	14.94	19.82	16.00	10.93	7.64
Furfurals	5-Methyl furfural	24.80	14.77	17.20	9.63	12.75	18.25	5.48	8.32
	5-Hydroxymethyl furfural	1.36	0.53	0.35	0.13	0.16	0.11	0.11	0.10
	Furfural	0.50	0.57	0.49	0.18	0.10	0.19	0.12	0.09
Aldehydes and ketones	3-Methyl-2-cyclopentene-1-one	0.02	0.01	0.00	0.79	0.03	0.05	0.03	0.02
	2-Cyclo-pentan-1-one	0.22	0.26	0.28	0.03	0.06	0.19	0.07	0.07
	Formaldehyde	0.04	0.04	0.04	0.10	0.03	0.44	0.14	0.01
	Acetaldehyde	0.19	0.05	0.08	0.04	0.11	0.20	0.05	0.08
	Acetone and propionaldehit	2.75	4.43	3.88	2.76	2.09	3.63	4.39	4.35
Phenols	Phenol	0.02	0.06	0.04	0.01	0.02	0.03	0.02	0.02
	m- & p-cresol	0.28	0.23	0.32	0.56	0.19	0.40	0.47	0.78
	o-cresol	0.04	0.38	0.21	2.57	0.10	1.87	0.25	0.26
	Resorcinol	0.05	0.07	0.07	0.04	0.01	0.03	0.00	0.01
	Catechol	0.03	0.09	0.08	0.02	0.03	0.07	0.02	0.06
	3-methoxy catechol	0.09	0.07	0.05	0.07	0.17	0.02	0.03	0.06
	methoxy benzene+4- methoxy phenol	3.62	3.99	5.44	3.12	1.86	2.72	2.98	3.98
	2-6 Di methoxy phenol	0.14	0.25	0.17	0.17	0.13	0.19	0.20	0.15
	2- methoxy phenol + 3- methoxy phenol	0.26	0.09	0.18	0.09	0.09	0.09	0.05	0.04
	4-methyl guaiacol	0.14	0.26	0.62	0.59	0.15	0.02	0.36	0.26
	3,4 methyl phenol	0.03	0.03	0.15	0.09	0.00	0.11	0.08	0.06
	4-vinyl guaiacol	0.02	0.03	0.10	0.07	0.10	0.22	0.32	0.27
	3,5 dimethyl phenol	0.13	0.04	0.23	0.25	0.04	0.34	0.45	0.32

Table 5.3.31 Concentrations of major organic compounds identified in liquid product from the gasification of pectin in relation to pressure for the reaction temperature of 600°C.

Yield (g/kg pectin)	Reaction pressure	210	285	360	430	205	280	355	440
	Catalyst, % 10	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Carboxylic acids									
	Glycolic acid	1.59	1.26	0.90	0.06	1.89	1.13	1.21	1.11
	Formic acid	3.50	3.19	3.03	5.11	7.61	9.16	8.94	13.58
	Acetic acid	24.81	27.93	19.50	12.58	27.14	17.89	10.00	12.86
Furfurals									
	5-Methyl furfural	30.93	27.37	9.42	20.97	24.02	23.42	7.34	11.91
	5-Hydroxymethyl furfural	1.47	0.80	0.07	0.05	0.17	0.14	0.12	0.11
	Furfural	0.80	0.64	0.51	0.14	0.10	0.16	0.13	0.07
Aldehydes and ketones									
	3-Methyl-2-cyclopentene-1-one	0.01	0.00	0.00	0.00	0.02	0.03	0.00	0.01
	2-Cyclo-pentan-1-one	3.65	0.16	0.35	0.01	0.10	0.12	0.07	0.03
	Formaldehyde	0.10	0.11	0.02	0.03	0.11	0.12	0.08	0.06
	Acetaldehyde	1.18	1.20	0.90	0.89	1.16	0.39	0.42	0.29
	Acetone and propionaldehit	0.06	0.01	0.00	0.01	0.00	0.02	0.06	0.01
Phenols									
	Phenol	0.28	0.08	0.00	0.01	0.00	0.04	0.22	0.00
	m- & p-cresol	0.17	0.01	0.01	0.01	0.01	0.01	0.00	0.01
	o-cresol	1.61	0.04	0.04	0.01	0.12	0.05	0.05	0.02
	Resorcinol	0.17	0.02	0.00	0.06	0.13	0.06	0.03	0.03
	Catechol	1.92	1.29	1.43	1.20	0.31	0.31	1.92	0.49
	3-methoxy catechol	0.10	0.11	0.18	0.26	0.03	0.17	0.17	0.22
	methoxy benzene+4- methoxy phenol	0.09	0.05	0.17	0.03	0.03	0.08	0.06	0.02
	2-6 Di methoxy phenol	0.38	0.01	0.01	0.01	0.02	0.01	0.01	0.01
	2- methoxy phenol + 3-methoxy phenol	0.31	0.00	0.00	0.01	0.00	0.01	0.02	0.00
	4-methyl guaiacol	0.07	0.00	0.01	0.01	0.00	0.00	0.42	0.00
	3,4 methyl phenol	0.00	0.00	0.00	0.00	0.01	0.00	0.60	0.00
	4-vinyl guaiacol	0.07	0.06	0.04	0.01	0.03	0.03	0.12	0.02
	3,5 dimethyl phenol	0.02	0.01	0.02	0.01	0.02	0.02	0.00	0.00

Table 5.3.32 Concentrations of major organic compounds identified in liquid product from the gasification of galacturonic acid in relation to catalyst and temperature.

Yield (g/kg galacturonic acid)	Reaction temperature (°C)	400	500	600	400	500	600	400	500	600
	Reaction pressure (atm)	186	335	385	230	350	420	222	352	430
	Catalyst, % 10	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	KOH	KOH	KOH
Carboxylic acids	Glycolic acid	8.29	2.23	2.03	0.18	0.29	0.00	0.16	0.90	0.29
	Formic acid	22.89	37.54	11.76	1.12	5.28	8.59	1.43	6.19	15.71
	Acetic acid	39.47	20.72	11.61	20.51	10.55	11.11	16.77	22.14	15.69
Furfurals	5-Methyl furfural	51.84	24.48	41.26	60.82	22.02	8.42	61.42	31.00	24.95
	5-Hydroxymethyl furfural	2.43	2.09	0.04	2.65	2.27	0.04	0.05	0.01	0.01
	Furfural	0.39	0.18	0.41	0.00	0.06	0.15	0.06	0.08	0.03
Aldehydes and ketones		0.05	0.00	0.02	0.09	0.00	0.00	0.05	0.00	0.00
	3-Methyl-2-cyclopentene-1-one									
	2-Cyclo-pentan-1-one	0.39	0.08	0.64	0.06	0.04	0.18	0.09	0.05	0.00
	Formaldehyde	0.02	0.02	0.06	0.01	0.01	0.00	0.02	0.02	0.00
	Acetaldehyde	0.46	0.11	0.74	0.08	0.07	0.13	0.01	0.02	0.06
	Acetone and propionaldehyde	5.18	0.00	0.00	0.00	0.81	2.33	0.00	0.00	0.13
Phenols	Phenol	0.01	0.01	0.01	0.03	0.00	0.01	0.01	0.01	0.00
	m-& p-cresol	0.00	1.70	0.23	0.54	0.05	0.19	0.12	0.07	0.03
	o-cresol	0.00	0.00	0.84	0.00	0.00	0.46	0.00	0.14	0.00
	Resorcinol	0.07	0.03	0.06	0.01	0.00	0.01	0.01	0.00	0.00
	Catechol	0.78	0.05	0.62	0.09	0.05	0.23	0.04	0.02	0.05
	3-methoxy catechol	0.05	0.05	0.02	0.03	0.02	0.01	0.00	0.04	0.01
	methoxy benzene+4- methoxy phenol	1.92	4.76	0.72	2.15	5.07	0.33	2.82	4.69	0.27
	2-6 Di methoxy phenol	0.77	0.31	0.44	0.32	0.14	0.20	0.21	0.14	0.14
	2- methoxy phenol + 3- methoxy phenol	0.31	0.12	0.11	0.15	0.03	0.07	0.11	0.04	0.08
	4-methyl guaiacol	0.24	0.34	0.01	0.43	0.17	0.01	0.23	0.16	0.03
	3,4 methyl phenol	0.11	0.00	0.00	0.00	0.16	0.00	0.03	0.18	0.00
	4-vinyl guaiacol	0.08	0.05	0.00	0.18	0.01	0.03	0.14	0.33	0.00
	3,5 dimethyl phenol	0.16	0.26	0.00	0.48	0.58	0.00	0.50	0.58	0.01
	Total Phenol (colorimetric)	4.97	6.82	1.47	5.36	8.54	0.70	5.80	8.29	0.89

Table 5.3.33 Concentrations of major organic compounds identified in liquid product from the gasification of galacturonic acid in relation to pressure for the reaction temperature of 400°C.

Yield (g/kg galacturonic acid)	Reaction pressure	205	270	345	425	205	275	345	420
	Catalyst, % 10	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Carboxylic acids									
	Glycolic acid	0.16	0.23	0.00	0.55	0.05	0.08	2.74	0.11
	Formic acid	3.81	1.33	0.14	2.50	0.62	1.34	4.03	7.32
	Acetic acid	58.91	9.74	12.32	9.95	15.07	15.21	12.50	13.85
Furfurals									
	5-Methyl furfural	0.00	39.48	22.73	21.72	58.85	55.50	49.11	48.80
	5-Hydroxymethyl furfural	1.09	0.55	0.32	0.07	0.14	0.12	0.07	0.01
	Furfural	0.45	0.55	0.36	0.26	0.16	0.04	0.03	0.03
Aldehydes and ketones									
	3-Methyl-2-cyclopentene-1-one	0.32	0.01	0.12	0.01	0.05	0.09	0.15	0.04
	2-Cyclo-pentan-1-one	0.16	0.44	1.17	1.16	0.03	0.14	0.14	0.07
	Formaldehyde	0.00	0.01	0.01	0.00	0.01	0.01	0.01	0.01
	Acetaldehyde	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
	Acetone and propionaldehyde	0.06	0.53	0.62	0.94	0.14	0.06	0.75	0.01
Phenols									
	Phenol	0.58	4.22	3.77	2.50	2.23	3.17	3.31	3.18
	m- & p-cresol	0.13	0.00	0.36	1.66	0.46	0.61	0.78	0.50
	o-cresol	0.21	0.00	0.16	0.00	1.71	0.00	0.19	0.13
	Resorcinol	0.05	0.25	0.09	0.05	0.01	0.00	0.00	0.00
	Catechol	0.49	2.17	6.04	2.53	0.01	0.06	0.05	0.13
	3-methoxy catechol	0.14	0.05	0.04	0.01	0.02	0.02	0.00	0.00
	methoxy benzene+4- methoxy phenol	2.18	2.07	1.95	1.93	2.27	1.60	1.75	1.74
	2-6 Di methoxy phenol	0.80	0.68	0.50	0.38	0.04	0.23	0.03	0.03
	2- methoxy phenol + 3- methoxy phenol	0.27	0.25	0.08	0.03	0.07	0.14	0.02	0.04
	4-methyl guaiacol	0.15	0.61	0.59	0.11	0.26	0.30	0.05	0.04
	3,4 methyl phenol	0.02	0.31	0.13	0.12	0.17	0.01	0.04	0.03
	4-vinyl guaiacol	0.26	0.33	0.18	0.18	0.22	0.11	0.10	0.07
	3,5 dimethyl phenol	0.28	0.17	0.08	0.05	0.55	0.42	0.33	0.23
	Total Phenol (colorimetric)	5.23	5.29	5.29	5.04	8.03	5.23	5.23	5.23

Table 5.3.34 Concentrations of major organic compounds identified in liquid product from the gasification of galacturonic acid in relation to pressure for the reaction temperature of 500°C.

Yield (g/kg galacturonic acid)	Reaction pressure	200	275	370	425	195	270	345	430
	Catalyst, % 10	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Carboxylic acids									
	Glycolic acid	0.12	0.19	0.02	0.02	0.04	0.00	0.04	0.00
	Formic acid	1.93	1.37	0.93	0.51	2.63	2.50	2.48	15.00
	Acetic acid	17.09	7.02	11.09	4.05	10.40	6.73	5.23	6.53
Furfurals									
	5-Methyl furfural	26.54	12.29	20.15	9.21	10.25	30.33	5.15	11.86
	5-Hydroxymethyl furfural	1.45	0.56	0.37	0.13	0.17	0.11	0.11	0.10
	Furfural	0.45	0.12	0.22	0.14	0.01	0.02	0.02	0.04
Aldehydes and ketones									
	3-Methyl-2-cyclopentene-1-one	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	2-Cyclo-pentan-1-one	0.01	0.00	0.02	0.00	0.01	0.05	0.02	0.03
	Formaldehyde	0.01	0.00	0.00	0.11	0.00	0.00	0.17	0.00
	Acetaldehyde	0.20	0.02	0.05	0.03	0.09	0.07	0.05	0.05
	Acetone and propionaldehit	0.42	4.10	2.89	2.47	0.84	2.59	3.22	4.19
Phenols									
	Phenol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
	m-& p-cresol	0.17	0.03	0.08	0.53	0.10	0.36	0.05	0.42
	o-cresol	0.00	0.23	0.25	2.98	0.00	2.42	0.19	0.13
	Resorcinol	0.04	0.01	0.07	0.04	0.01	0.01	0.00	0.01
	Catechol	0.01	0.08	0.06	0.01	0.01	0.03	0.02	0.05
	3-methoxy catechol	0.11	0.06	0.06	0.09	0.07	0.01	0.02	0.07
	methoxy benzene+4- methoxy phenol	4.10	3.26	5.04	4.15	2.19	2.86	1.81	3.44
	2-6 Di methoxy phenol	0.16	0.22	0.11	0.22	0.08	0.23	0.16	0.17
	2- methoxy phenol + 3- methoxy phenol	0.33	0.08	0.20	0.11	0.11	0.12	0.06	0.04
	4-methyl guaiacol	0.12	0.01	0.30	0.28	0.01	0.01	0.01	0.17
	3,4 methyl phenol	0.01	0.00	0.11	0.06	0.00	0.14	0.02	0.01
	4-vinyl guaiacol	0.00	0.02	0.10	0.07	0.13	0.26	0.42	0.36
	3,5 dimethyl phenol	0.16	0.02	0.26	0.28	0.05	0.43	0.60	0.42
	Total Phenol (colorimetric)	5.53	6.57	6.57	7.33	8.20	1.79	1.79	7.97

Table 5.3.35 Concentrations of major organic compounds identified in liquid product from the gasification of galacturonic acid in relation to pressure for the reaction temperature of 600°C.

Yield (g/kg galacturonic acid)	Reaction pressure	195	280	345	428	200	270	345	420
	Catalyst, % 10	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Carboxylic acids									
	Glycolic acid	0.13	0.18	0.00	0.06	0.05	0.06	0.06	0.03
	Formic acid	3.12	1.93	0.00	2.67	6.82	7.80	3.30	9.59
	Acetic acid	11.05	16.77	4.17	11.20	17.96	15.12	6.98	14.86
Furfurals									
	5-Methyl furfural	33.39	31.25	6.22	22.01	31.35	30.83	6.86	15.83
	5-Hydroxymethyl furfural	1.56	0.85	0.07	0.05	0.18	0.14	0.12	0.11
	Furfural	0.13	0.18	0.20	0.17	0.02	0.11	0.02	0.01
Aldehydes and ketones									
	3-Methyl-2-cyclopentene-1-one	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	2-Cyclo-pentan-1-one	0.00	0.01	0.00	0.00	0.00	0.03	0.02	0.00
	Formaldehyde	0.00	0.00	0.01	0.00	0.00	0.01	0.13	0.00
	Acetaldehyde	0.03	0.08	0.01	0.03	0.04	0.04	0.02	0.02
	Acetone and propionaldehit	0.05	0.25	0.23	0.20	0.34	0.05	0.11	0.09
Phenols									
	Phenol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	m- & p-cresol	0.00	0.00	0.00	0.00	0.00	0.00	0.06	0.00
	o-cresol	0.00	0.00	0.00	0.00	0.00	0.00	0.25	0.00
	Resorcinol	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.00
	Catechol	0.02	0.04	0.03	0.01	0.06	0.05	0.02	0.00
	3-methoxy catechol	0.04	0.02	0.00	0.06	0.16	0.06	0.03	0.02
	methoxy benzene+4- methoxy phenol	0.20	0.42	0.61	0.37	0.37	0.28	2.41	0.49
	2-6 Di methoxy phenol	0.02	0.06	0.24	0.28	0.03	0.19	0.22	0.27
	2- methoxy phenol + 3- methoxy phenol	0.03	0.06	0.22	0.02	0.04	0.07	0.08	0.02
	4-methyl guaiacol	0.03	0.00	0.00	0.00	0.02	0.00	0.01	0.00
	3,4 methyl phenol	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00
	4-vinyl guaiacol	0.00	0.00	0.00	0.01	0.00	0.00	0.56	0.00
	3,5 dimethyl phenol	0.00	0.00	0.00	0.00	0.00	0.00	0.80	0.00
	Total Phenol (colorimetric)	2.05	2.10	2.10	2.74	1.92	5.23	5.23	0.70

5.4 Evaluation of Possible Structural Changes in Activated Carbon Catalysts after Supercritical Water Gasification

Activated carbon (AC) can be used as a catalyst by itself or as a catalyst support. Low temperature SCWG can not be enhanced by using carbon, but for high temperature SCWG, activated carbon is a good heterogeneous catalyst in terms of cost. But for hydrogen production, the AC itself has low catalytic activity compared with the Ni/AC catalyst (Lee et al., 2009). The surface area and pore size of the activated carbons values are in the range of 800-1500 m²/g and 0.5 and 1 nm respectively.

Table 5.4.1 shows the change in carbon content, BET surface area and total pore volume of the AC catalysts after using in the supercritical water gasification of xylose at 600°C. The carbon content of AC, Ru/AC and Ni/AC increased when the catalysts were used in the SCWG. Coke could be formed during the xylose supercritical water gasification, contributing to increase in the carbon content. When the activated carbon catalysts were used in the supercritical water gasification experiments, BET surface area significantly decreased. Lee et al. and Antal et al. also observed significant reduction in BET surface area after using as a catalyst in the SCWG (Lee 2009, Antal 2000). The BET surface area of fresh AC (~1000 m²/g) was smaller than typical activate carbons (>1500 m²/g). Also this small BET surface area had relatively high total pore volume of 0.90cm³/g. Total pore volume decreased significantly when the activated carbon catalysts were used in the supercritical water gasification of xylose at 600°C.

SEM images for the surface of the fresh and spent AC, Ni/AC and Ru/AC catalysts are shown in Figure 5.4.1 at a magnification of 10000. It can be seen from the image that, the surface structure of the activated carbon had little change after using in the supercritical water gasification of xylose at 600°C and adding Ni and Ru to the activated carbon caused their surface structures to change much more during spending. These results are in harmony with carbon content given in Table 5.2.1.

Table 5.4.1 Change in physical properties of the AC. Ni/AC and Ru/AC catalysts after used in the SCWG of xylose at 600°C.

Sample	Carbon content (wt %)	BET surface area (m ² /g)	Total pore volume (cm ³ /g)
Fresh AC	93.18	996	0.90
Fresh Ni/AC	75.24	519	0.44
Fresh Ru/AC	70.05	380	0.34
Spent AC at 600°C	95.10	48	0.04
Spent Ni/AC at 600°C	80.08	11	0.01
Spent Ru/AC at 600°C	87.92	150	0.10

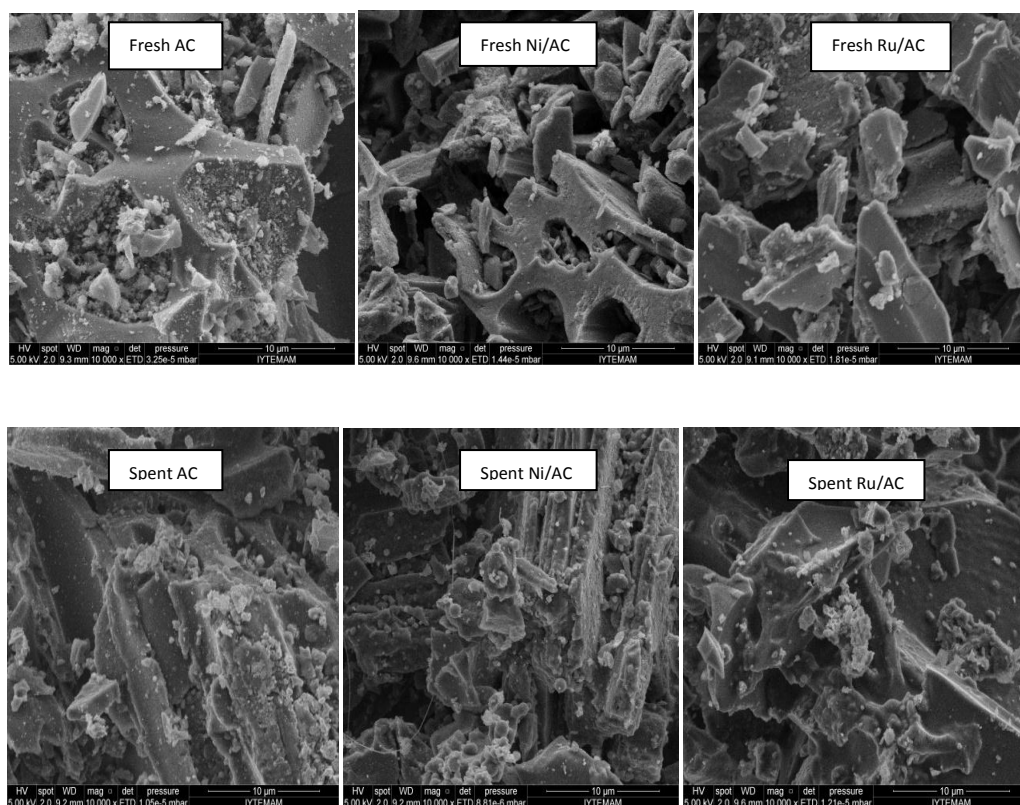


Figure 5.4.1 SEM images of the fresh and spent catalysts at 600°C: fresh AC, fresh Ni/AC, fresh Ru/AC, spent AC, spent Ni/AC and spent Ru/AC.

6.0 Conclusion

Due to the environmental considerations, i.e. increasing atmospheric toxic gases (CO_2 , SO_2 , NO_x and other pollutants) concentrations from the combustion of fossil fuels and the dependence on fossil fuels in the world increases, researches of alternative energy sources are getting more attention. Biomass is renewable, readily available, only carbon based material in renewable energy groups and also carbon-neutral feedstock that can be converted into fuels and chemicals. Since biomass feedstocks generally have high moisture contents and removing this water prior to the conventional thermochemical technologies (gasification, combustion, pyrolysis and liquefaction) increases the cost needed to convert biomass to the gas or liquid fuels (Zhang et al., 2010, DiLeo et al., 2007). For this reason, supercritical water gasification is an excellent method for wet biomass. The principle of this method is to convert wet biomass into gas using high temperatures and pressures above the critical point (22.1 MPa and 374°C).

The potential of hot compressed water in the sub-and supercritical state is considered to be unique, because it utilizes water as a solvent and as a reactant at the same time. Advantages include water's role as a reaction solvent, high reactivity, eliminating the necessity for drying the biomass, short residence time required to complete gasification, since product gas obtained as compressed, to compress e.g. for transportation is not necessary, less tar and coke formation (Huelsman et al., 2013, Kruse 2005)

By the effect of temperature and pressure conditions, physical properties of the water such as density, viscosity, dielectric constant and ion product can be varied. Moreover, supercritical water generates additional hydrogen through reforming reactions and produces gas low in carbon monoxide (Goodwin et al., 2011).

Biomass is mainly composed of cellulose, hemicellulose, lignin, and extractives and the compositions vary depending on the source of the biomass. These major structural components have rough compositions of 30-50% of cellulose, 20-40% of hemicelluloses, 15-25% of lignin and 1-3% extractives. The ratios of these monomers can change quite dramatically

for different feedstock sources. Many studies on the degradation of biomass in near- and supercritical water have been published. Since biomass is a complex mixture of variable composition, most studies were carried out with cellulose, glucose as a model substance for cellulose, lignin, phenol as a model substance for lignin. There are some studies describing hydrothermal gasification of the hemicellulose.

In this study, xylose, arabinose and pectin as model compound for the hemicellulose, tannic acid, gallic acid, 1,2,3 trihidroksibenzene and 1,3,5 trihidroksibenzene for extractives were studied. Hydrothermal gasification was performed in a batch reactor system at temperature and pressure ranges of 400-600°C and 20-42.5MPa. Also xylose, arabinose and tannic acid were studied at 400, 500 and 600°C in the presence of, KOH, activated carbon-Ni and activated carbon-Ru. Gallic acid, 1,2,3 trihidroksibenzene, 1,3,5 trihidroksibenzene and pectin were studied at 400, 500 and 600°C in the presence of K₂CO₃ and KOH. Totally 292 of hydrothermal gasification experiments were performed in a batch reactor system. Xylose and arabinose studies were completed in the TUBITAK Project 109M284 (Saglam, 2013). Galacturonic acid results, that have been completed in the TUBITAK Project (Saglam, 2013), were used to compare with the pectin results. Since the experiments were repeated at least three times, the average yield was able to evaluate and the reproducibility confirm. The objective of this study was to elucidate the effect of the high reaction temperature, high pressure and catalyst on the gas and liquid product distribution.

The influences of temperature, pressure and catalyst were examined in relation to the maximum yields of the H₂ and CH₄ gases and the liquid products of furfurals, aldehydes and carboxylic acids by gas and liquid chromatographic techniques. The compositions of the products are sensitive to temperature, pressure and the catalytic activity. The effect of temperature on gaseous product composition is dominant compared with the effect of pressure. This situation may be explained by variation of dielectric constant of water with temperature and pressure. The dielectric constant of water was considerably decreased by increasing the temperature while slightly increased by increasing the pressure.

An increase in the temperature of hydrothermal gasification is favored the production of larger amount of gas product and small amount of residue fractions. The highest carbon gasification efficiencies were found at 600°C in the presence of KOH and K₂CO₃. When three main types of catalysts (alkaline, metals and carbon) used in the supercritical water gasification process, improve the gasification efficiency and decreases the required temperature for the gasification.

If the temperature was increased, the obtained results can be summarized for supercritical water gasification of xylose, arabinose, tannic acid, gallic acid, 1,2,3 trihidroksibenzene, 1,3,5 trihidroksibenzene and pectin as below;

- Gas yield increased,
- Amount of the desired gaseous products like H₂ and CH₄ and energy source or valuable chemicals like C₂-C₄ increased, CO₂ decreased,
- Amount of the CO decreased as a result of water-gas shift reaction in supercritical water,
- Variety and amount of the organic compounds in aqueous product decreased,
- Amount of coke decreased,
- Presence of catalyst in SCWG improved the results.

With increasing pressure and at constant temperatures of 400, 500 and 600°C the obtained results can be summarized for supercritical water gasification of xylose, arabinose, tannic acid, gallic acid, 1,2,3 trihidroksibenzene, 1,3,5 trihidroksibenzene and pectin;

- Hydrogen amount has a tendency to increase slightly with decreasing pressure. Hydrogen yield reached maximum values at the highest temperature 600°C and at the minimum pressure 200 atm. The results show that H₂ yield increases significantly when the catalysts are used.
- Methane yield increased with increasing temperature and pressure. Methane yield was found to be maximum at 600 °C and 425 atm.
- Carbon dioxide yields decrease with increasing pressure at constant temperature.

Gas yield and gas product distribution results obtained by the temperature, pressure and catalyst effects can be summarized for supercritical water gasification of xylose and arabinose:

- Gas yields, H₂, CH₄, CO₂ and C₂-C₄ yields were obtained at close values.

Gas yield and gas product distribution results obtained by the temperature, pressure and catalyst effects can be summarized for supercritical water gasification of tannic acid and gallic acid:

- Gas yields were obtained at close values,
- H₂ yield of tannic acid was more than that of gallic acid,
- CH₄ yield of tannic acid was more than that of gallic acid,
- CO₂ yield of tannic acid was more than that of gallic acid,
- C₂-C₄ yields of gallic acid were more than that of tannic acid.

Gas yield and gas product distribution results obtained by the temperature, pressure and catalyst effects can be summarized for supercritical water gasification of phloroglucinol and pyrogallol:

- Gas yield of phloroglucinol was more than that of pyrogallol,
- H₂ yield of pyrogallol was more than that of phloroglucinol,
- CH₄ yield of phloroglucinol was more than that of pyrogallol,
- CO₂ yield of pyrogallol was more than that of phloroglucinol,
- C₂-C₄ yields of pyrogallol were more than that of phloroglucinol.

Gas yield and gas product distribution results obtained by the temperature, pressure and catalyst effects can be summarized for supercritical water gasification of pectin and galacturonic acid:

- Gas yields were obtained at close values,
- H₂ yield of pectin was more than that of galacturonic acid,
- CH₄ yield of pectin was more than that of galacturonic acid,
- CO₂ of galacturonic acid was more than that of pectin,
- C₂-C₄ yields of pectin were more than that of galacturonic acid.

The influence of temperature, pressure and catalyst on liquid product formation were examined during supercritical water gasification of the selected model compounds; xylose, arabinose, tannic acid, gallic acid, phloroglucinol, pyrogallol, pectin and galacturonic acid hydrothermal gasification. The aqueous phase contains large number of different compounds. For the aqueous phase, the analysis mainly were focused on identification of key compounds like carboxylic acids, furfurals, phenols, aldehydes, ketones and their alkylated derivatives. Total carboxylic acids (formic acid, acetic acid), total furfurals (furfural, 5-hydroxymethyl furfural, 5-methyl furfural), total phenols (phenol, o-m-p cresols, resorcinol, cat-echol, 3-methoxycatechol, methoxybenzene, 2-methoxyphenol, 3-methoxyphenol, 4-methoxyphenol, 2,6 dimethoxyphenol, 4-methyl guaiacol, 3,4 dimethyl phenol, 3,5 dimethyl phenol and 4-vinyl guaiacol), total aldehydes and ketones (formaldehyde, acetaldehyde, acetone, propionaldehyde, 3-methyl-2-cyclopenten-1-one, 2-cyclopenten-1-one). The variety of the aqueous product contributed to the TOC (Total organic carbon) amount of the liquid phase. TOC value decreased with increasing temperature, as the formed aqueous products converted into gaseous products. Also in the presence of catalysts, TOC content was lower than in the absence of a catalyst.

A reaction pathway was proposed to investigate the liquid intermediate products obtained from xylose by retro-aldol (RA), dehydration (DH), Lobry de Bruyn-Alberta van Ekenstein Transformation (LBET), tautomerization (Taut), beuzilic acid rearrangement (BR) and oxidation (Ox) reactions. The proposed reaction mechanism of xylose can offer a different perspective to gain further insights into the reaction pathways of the hemicellulose depolymerization. The highest measured concentration of retro aldol reaction product was acetic acid and dehydration product was 5-methyl furfural. Both retro-aldol and dehydration reactions of xylose decreased by increasing pressure at the constant temperature conditions. The deficiency in the literature was eliminated by clarifying the reaction mechanism and the attitude in the supercritical water of the hemicellulose and extractive model compounds.

REFERENCES

- Aida, T. M., Sato, Y., Watanabe, M., Tajima, Kiyohiko., Nonakaa, Toshiyuki., Hattori, H., and Arai, K., 2007**, Dehydration of d-glucose in high temperature water at pressures up to 80MPa, *J. of Supercritical Fluids*, 40:381–388 pp.
- Antal, Jr. M.J., Adschiri, T., Ekbom, T., Garcia, A., Matsumura, Y., Minowa, T., Nuessle, F., Sakurai, M., and Xu, X., 1996**, Hydrogen Production from High-Moisture Content Biomass in Supercritical Water. *Proceedings of the 1996 U.S. DOE Hydrogen Program Annual Review*, 1: 499-511 pp.
- Antal, Jr. M.J., Allen, S., Lichwa, J., Schulman, O., and Xu, X., 1999**, Hydrogen Production from High Moisture Content Biomass in Supercritical Water, *Proceedings of the 1999 U.S. DOE Hydrogen Program Review*, 1-24 pp.
- Antal, M. J. Jr., Allen, S.G., Schulman, D., and Xu, X., 2000**, Biomass Gasification in Supercritical Water, *Ind. Eng. Chem. Res*, 39:4040-4053 pp.
- Antal, M.J., Mok, W.S.L., and Richards, G.N., 1990**, Kinetic-studies of the reactions of ketoses and aldoses in water at high-temperature. 1. Mechanism of formation of 5-(hydroxymethyl)-2-furaldehyde from d-fructose and sucrose, *Carbohydr. Res*, 199:91–109 pp.
- Azadi, P., and Farnood, R., 2011**, Review of heterogenous catalysts for sub and supercritical water gasification of biomass and wastes, *International Journal of Hydrogen Energy*, 1-13 pp.
- Azadi, P., Khan, S., Strobel, F., Azadi, F., and Farnood, R., 2012**. Hydrogen production from cellulose, lignin, bark and model carbohydrates in supercritical water using nickel and ruthenium catalysts, *Applied Catalysis B: Environmental*, 117–118:330– 338 pp.
- Balasundram, N., Sundram, K., and Samman, S., 2006**, Phenolic compounds in plants and agri-industrial by-products: Antioxidant activity, occurrence, and potential uses, *Food Chemistry*, 99:191-203 pp.

REFERENCES (Continued)

- Barış, K., and Kucukali, S.,** 2012, Availability of renewable energy sources in Turkey: Current situation, potential, government policies and the EU perspective, *Energy Policy* 42:377–391 pp.
- Basu, P., and Mettanan, V.,** 2009, Biomass Gasification in Supercritical Water- A Review, *International Journal of Chemical Reactor Engineering*.
- Behnia, I.,** 2013, Treatment of aqueous biomass and waste via supercritical water gasification for the production of CH₄ and H₂, Master Thesis, The University of Western Ontario, Canada.
- Bobleter, O.,** 1994, Hydrothermal degradation of polymers derived from plants, *Prog. Polym. Sci*, 19:797-841 pp.
- Brahmachari, G., and Gorai, D.,** 2006, Progress in the research on naturally occurring flavones and flavonols: An overview. *Current Organic Chemistry*, 10:873-898 pp.
- Bridgwater, A.,** 2001, Thermal conversion of biomass and waste: the status, Bio-Energy Research Group, Aston University, Birmingham.
- Browning, B.L.,** 1963, The Chemistry of Wood, The Institute of Paper Chemistry, Appleton, Wisconsin.
- Carrier, M., Loppinet-Serani, A., Absalon, C., Aymonier, C., and Mench, M.,** 2012, Degradation pathways of holocellulose, lignin and α -cellulose from *Pteris vittata* fronds in sub- and super critical conditions, *Biomass Bioenerg*, 43:65-71 pp.
- Castello, D.,** 2013, Supercritical Water Gasification of Biomass, Doctoral Thesis in Environmental Engineering, Trento University, Italy.
- Chen, S.F., Mowery, R.A., Castleberry, V.A., Walsum, G.P., and Chambliss, C.K.,** 2006, High-performance liquid chromatography method for simultaneous determination of aliphatic acid, aromatic acid and neutral degradation products in biomass pretreatment hydrolysates, *Journal of Chromatography A*, 1104:54-61 pp.

REFERENCES (Continued)

Chrastil, J., 1982, Solubility of Solids and Liquids in Supercritical Gases, *Journal of Supercritical Chemistry*, 86: 3016-3021 pp.

Corella, J., Aznar, M.P., Gil, J., and Caballero, M.A., 1999, Biomass gasification in fluidised bed: where to locate the dolomite to improve gasification, *Energy and Fuels* 13:1122 pp.

Cortright, R.D., Davda, R.R., Dumesic, J.A., 2002, Hydrogen from catalytic reforming of biomass-derived hydrocarbons in liquid water. *Nature*, 418:964-967 pp.

Da Rosa, A.V., 2005, *Fundamentals of Renewable Energy Processes*, Elsevier Inc, Massachusetts.

Dahmen, D., and Dinjus, E., 2010, Vorlesung Biomasse–nicht nur eine Ergänzung zu fossilen erneuerbarer Energieträgern, KIT, Germany.

Dahmen, N., Henrich, E., Dinjus, E., and Weirich, F., 2012, The bioliq bioslurry gasification process for the production of biosynfuels, organic chemicals, and Energy, *Energy, Sustainability and Society*, 2:3.

Deffeyes, K.S., 2005, *Beyond Oil*, Hill and Wang, New York.

DiLeo, G.L., Neff, M.E., Kim, S., and Savage, P.E., 2007, Gasification of Guaiacol and Phenol in Supercritical Water, *Energy Fuels*, 2:2340-2345 pp.

Dunn, S., 2002, Hydrogen futures: toward a sustainable energy system, *International Journal of Hydrogen Energy*, 27:235–264 pp.

EIE, 2009, General Directorate of Electrical Power Resources Survey and Development Administration, Wind Power Plants Operated in Turkey, www.eie.gov.tr.

EIE, 2010, General Directorate of Electrical Power Resources Survey and Development Administration, [/http://www.eie.gov.tr](http://www.eie.gov.tr)S.

Elliott, D.C., 2008, Catalytic hydrothermal gasification of biomass. *Biofuels, Bioproducts and Biorefining*, 2:254-265 pp.

REFERENCES (Continued)

- Elliott, D.C., and John, S. Jr. L.**, 2004, Aqueous catalyst systems for the water-gas shift reaction, Comparative catalyst studies, *Ind. Eng. Chem. Res.*, 43:502-508 pp.
- Eurocoal**, 2010, European Association for Coal and Lignite, <http://www.eurocoal.org/pages/layout1sp.php?idpage=475>.
- Fengel, D., and Wegener, G.**, 1989, *Wood. Chemistry, Ultrastructure, Reactions*, Walter de Gruyter, Berlin, Germany, 613 p.
- Fernendo, L., and Resende, P.**, 2009, Supercritical Water Gasification of Biomass, the thesis of Doctor of Philosophy in the University of Michigan.
- Freudenberg, K., and Neish, A.C.**, 1968, *Constitution and Biosynthesis of Lignin*, Springer, G.F., Kleinzeller, A., Springer-Verlag, New York. 129 pp.
- Garrote, G., Dominguez, H., and Parajo, J.C.**, 1999, Hydrothermal processing of lignocellulosic materials. *Holz Als Roh-Und. Werkstoff*, 57:191-202 pp.
- Goodwin, A.K., and Rorrer, G.L.**, 2010, Reaction rates for supercritical water gasification of xylose in a micro-tubular reactor, *Chemical Engineering Journal* 163:10–21 pp.
- Goodwin A.K., and Rorrer, G.L.**, 2011, Modeling of Supercritical Water Gasification of Xylose to Hydrogen-Rich Gas in a Hastelloy Microchannel Reactor, *Ind Eng Chem Res*, 50:7172–82 pp.
- Guo, L.J., Lu, Y.J., Zhang, X.M., Ji, C.M., Guan, Y., and Pei, A.X.**, 2007, Hydrogen production by biomass gasification in supercritical water: a systematic experimental and analytical study, *Catalysis Today*, 129:275-286 pp.
- Hemmes, K., Groot, A. D., and Uil, H.D.**, 2003, Bio-H₂; Application potential of biomass related hydrogen production technologies to the Dutch energy infrastructure of 2020 -2050, Report ECN-C--03-028.
- Henrich, E., Dahmen, N., and Dinjus, E.**, 2009, Cost estimate for biosynfuel production via biosyncrude gasification, *Biofuels, Bioproducts, Biorefining*, 3:28-41 pp.

REFERENCES (Continued)

Himmel, M.E., Baker, J.O., and Overend, R.P., 1993, Pretreatment of Lignocellulosic Biomass in Enzymatic conversion of biomass for fuel production, American Chemical Society, Washington: D.C McMillan JD.

Hodgson, P.E., 1999, Nuclear Power, Energy and the Environment, Imperial College Press, London.

Huelsman, C.M., and Savage, P.E., 2013, Reaction pathways and kinetic modeling for phenol gasification in supercritical water, J Supercrit Fluids, 81:200-209 pp.

Hydrogen Association, Evers, 2008, <http://decarboni.se/publications/ccs-roadmap-industry-high-purity-co2-sources-sectoral-assessment-%E2%80%93-final-draft-report-1>.

International Energy Outlook, 2005, Energy Information Administration: Washington D.C, <https://www.hsdl.org/?view&did=15905>.

Joseph, B.B., Jacqueline, J.B., Anthony, V.C., and Ronald, T.R., 2010, Synthesis of Furfural from Xylose and Xylan, Weinheim: WILEY.

Kamm, B., Gruber, P.R., and Kamm, M., 2006, Biorefinery Systems-An Overview, in Biorefineries-Industrial Processes and Products, Wiley-VCH Verlag GmbH & Co, Weinheim.

Kankanamge, A.I.R., 2013, Xylan depolymerisation under subcritical water conditions, the thesis of Doctor of philosophy, Sydney University.

Kersten, S.R.A., Potic, B., Prins, W., and Van Swaaij, W.P.M., 2006, Gasification of Model Compounds and Wood in Hot Compressed Water, Ind Eng Chem Res, 45: 4169 pp.

Klingler, D., 2006, Energetische Nutzung von feuchter Biomasse in überkritischem wasser, Dissertation, Technischen Universität Darmstadt, Darmstadt.

REFERENCES (Continued)

- Koç, E., and Şenel, M.C.,** 2013, The State of Energy in World and Turkey - General Evaluation, *Mühendis ve Makina*, 54:32-44 pp.
- Kruse, A., Krupka, A., Schwarzkopf, V., Gamard, C., and Henningsen, T.,** 2005, Influence of Proteins on the Hydrothermal Gasification and Liquefaction of Biomass. 1. Comparison of Different Feedstocks, *Ind. Eng. Chem. Res.*, 44, 3013-3020 pp.
- Kruse, A.,** 2005, Biomass gasification in supercritical water: Key compounds as a tool to understand the influence of biomass components, Joint 20th AIRAPT–43th EHPRG, June 27–July 1, Karlsruhe/Germany.
- Kruse, A.,** 2008, Supercritical water gasification, *Biofuels Bioproducts and Biorefining*, 2:415-437 pp.
- Kruse, A., Dinjus, E.,** 2007, Review; Hot compressed water as reaction medium and reactant Properties and sythesis reactions, *J of Supercritical Fluids*, 39: 362-380 pp.
- Kruse, A., and Gawlik, A.,** 2003, Biomass Conversion in Water at 330-410°C and 30-50 MP, Identification of Key Compounds for Indicating Different Chemical Reaction Pathways, *Ind. Eng. Chem. Res.*, 42, 267-279 pp.
- Laine, C.,** 2005, Structures of hemicelluloses and pectins in wood and pulp, the thesis of Doctor of science in technology Helsinki University of Technology Finland.
- Lee, J.G., Kim, M.S., and Ihm, S.K.,** 2002, Gasification of glucose in supercritical water, *Ind Eng Chem Res*, 41(5):1182-1188 pp.
- Lee, I.G., and Ihm, S.K.,** 2009, Catalytic Gasification of Glucose over Ni/Activated Charcoal in Supercritical Water, *Ind. Eng. Chem. Res.*, 48:1435–1442 pp.
- Lu, Y., Guo, L., Zhang, X., and Ji, C.,** 2005, Hydrogen production by supercritical water gasification of biomass: Explore the way to maximum hydrogen yield and high carbon gasification efficiency, *International Journal of Hydrogen Energy*, 37:3177-3188 pp.

REFERENCES (Continued)

Lu, Y.J., Guo, L.J., Ji, C.M., Zhang, X.M., Hao, X.H., and Yan, Q.H., 2006, Hydrogen production by biomass gasification in supercritical water: A parametric study, *International Journal of Hydrogen Energy*, 31:822-831 pp.

Malhotra, A., 2006, Introduction, Thermodynamic properties of supercritical steam, Steam Center Publisher, Jaipur.

Manarungson, S., Mok, W.S., and Antal Jr., M.J., 1990, Hydrogen Production by Gasification of Glucose and Wet Biomass in Supercritical Water, *Hydrogen Energy Progress VIII, Proceedings of the 8th World Hydrogen Energy Conference*, Honolulu Hawaii, 345-355 pp.

Marshall, W.L., and Franck, E.U., 1981, Ion product of water substance, 0-1000°C, 1-10,000 bars, New international formulation and its background, *Journal of Physical and Chemical Reference Data*, 10:295-304 pp.

Matsumura, Y., 2002, Evaluation of Supercritical Water Gasification and Biomethanation for Wet Biomass Utilization in Japan, *Energy Convers. Manage.*, 43: 1301-1310 pp.

Matsumura, Y., Adschiri, T., Xu, S., Garcia, A., and Antal, Jr. M.J., 1997a, Reaction Rate of Activated Carbon with Supercritical Water. The 4th International Symposium on Supercritical Fluids, Sendai, Japan, May 11-14:555-568 pp.

Matsumura, Y., Minowa, T., Potic, B., Kersten, S.R.A, Prins, W., Swaaij, W.P.M., Beld, B., Elliot, D.C., Neuenswander G.G., Kruse, A., and Antal, Jr M.J., 2005, Biomass gasification in near- and super-critical water: Status and prospects, *Biomass & Bioenergy*, 29: 269-292 pp.

Matsumura, Y., Xu, X., Antal, Jr. M.J., 1997b, Gasification Characteristic of an Activated Carbon in Supercritical Water, *Carbon* 35:819-824 pp.

REFERENCES (Continued)

Mavi Kitap, 2011, Enerji ve Tabii Kaynaklar Bakanlığı İle Bağlı ve İlgili Kuruluşlarının Amaç ve Faaliyetleri, Ankara, http://www.enerji.gov.tr/File/?path=ROOT%2F1%2FDocuments%2FMavi+Kitap%2FMavi_Kitap_2011.pdf

Milne, T.A., Abatzoglou, N., and Evans R.J., 1998, .Biomass gasifier tars: their nature, formation, and conversion, National Renewable Energy Laboratory Technical Report.

Minowa, T. and Fang, Z., 1998, Hydrogen Production from Cellulose in Hot Compressed Water Using Reduced Nickel Catalyst: Product Distribution at Different Reaction Temperature. Journal of Chemical Engineering of Japan, 31:488-491 pp.

Minowa, T., and Inoue, S., 1999, Hydrogen Production from Biomass by Catalytic Gasification in Hot Compressed Water. Renewable Energy 16: 1 114-1117 pp.

Minowa, T., and Ogi, T., 1998, Hydrogen Production from Cellulose Using a Reduced Nickel Catalyst, Catalysis Today, 45:411-416 pp.

Minowa, T., Ogi, T., Dote, Y., and Yokoyama, S., 1994, Methane Production from Cellulose by Catalytic Gasification, Renewable Energy, 813-815 pp.

Minowa, T., Ogi, T., and Yokoyama, S., 1997, Hydrogen Production from Lignocellulosic Materials by Steam Gasification Using a Reduced Nickel Catalyst, Developments in Thermochemical Biomass Conversion, 2:932-941 pp.

Minowa, T., Ogi, T., and Yokoyama, S.Y., 1995a, Hydrogen Production from Wet Cellulose by Low Temperature Gasification Using a Reduced Nickel Catalyst, Chemistry Letters: 937-938 pp.

Minowa, T., Ogi, T., and Yokoyama, S.Y., 1995b, Effect of Pressure on Low Temperature Gasification of a Cellulose into Methane Using Reduced Nickel Catalyst and Sodium Carbonate, Chemistry Letters, 285-286 pp.

REFERENCES (Continued)

Modell, M., 1977, Reforming of Glucose and Wood at the Critical Conditions of Water, American Society of Mechanical Engineers, July 11-14:8 p.

Modell, M., 1985, Gasification and Liquefaction of Forest Products in Supercritical Water. Fundamentals of Thermochemical Biomass Conversion, Elsevier Applied Science: 95-119 pp.

Modell, M., Reid, R.C., and Amin, S., 1978, Gasification Process. U.S. Patent 4, 113, 446. Sept.

Mok, W.S.L., and Antal, Jr. M.J., 1992, Uncatalyzed Solvolysis of Whole Biomass Hemicellulose by Hot Compressed Liquid Water, Ind. Eng. Chern. Res, 31: 1157-1161 pp.

Montilva P.M.D., 2007, Die vergasung von realer biomass in überkritischem wasser, Dr. Ing. Fakultät der Chemieingenieurwesen Universität Karlsruhe, Germany.

Mozaffarian, M., Deurwaarder, E. P., Kersten, S.R.A., 2004, Green gas (SNG) production by supercritical gasification of biomass: <http://www.ecn.nl/docs/library/report/2004/c04081.pdf>

Nanou, P., 2013, Biomass gasification for the production of methane, the Thesis of Doctor of Philosophy, University of Twente, Netherlands.

Narvaez, I., Corella, J., and Orio, A., 1997, Fresh tar (from a biomass gasifier) elimination over a commercial steam-reforming catalyst. Kinetics and effect of different variables of operation, Industrial and Engineering Chemistry Research, 36: 317 pp.

Nascimento, R. F., Marques, J. C., Neto, B. S. L., Keukeleire, D. D., and Franco, D.W., 1997, Qualitative and quantitative high-performance liquid chromatographic analysis of aldehydes in Brazilian sugar cane spirits and other distilled alcoholic beverages, J. Chromatogr A, 782:13-23 pp.

REFERENCES (Continued)

- Ni, M., Leung, D.Y.C., Leung, M.K.H., and Sumathy, K.,** 2006, An overview of hydrogen production from biomass, *Fuel Processing Technology*, 87: 461-472 pp.
- Olgun, H.,** 2013, Status of bioenergy in Turkey, Workshop on International cooperation in the field of bioenergy, 22-24 October, Moscow, Russia.
- Onken, U., and Behr A.,** 1996, *Chemische Prozeßkunde Ban 3*, Georg Thieme Verlag Stuttgart-New York.
- Pacheco, F.L.,** 2009, Supercritical Water Gasification of Biomass, the Thesis of Doctor of Philosophy, Michigan University, United States.
- Peterson, A.A., Vogel, F., Lachance, R.P., Fröling, M., Antal, Jr. M.J., Tester, J.,** 2008, Thermochemical biofuel production in hydrothermal media: a review of sub- and supercritical water technologies. *Energy Environmental Science*, 1:32–65 pp.
- Polat, T., Yalçın, A.H., and Şahin, H.M.,** 2012, Hidrojenin Nükleer Enerji ile Üretim Yollarının İncelenmesi, *Journal of Polytechnic* 15:49-69 pp.
- Potic B.,** 2006, Gasification of biomass in supercritical water, the thesis was executed under the Netherlands organization for scientific research, the Netherlands.
- Qian, X., Nimlos, M.R., Davis, M, Johnson, D.K., and Himmel, M.E.,** 2005, Ab initio molecular dynamics simulations of b-D-glucose and b-D-xylose degradation mechanisms in acidic aqueous solution, *Carbohydrate Research*, 340:2319-2327 pp.
- Ramsurn, H.,** 2013, Gasification, Liquefaction and Deoxy-Liquefaction of Switchgrass using Sub- and Supercritical Water, the thesis of Doctor of Philosophy, Auburn, Alabama.

REFERENCES (Continued)

Resende, F., Fraley, S., Berger, M., and Savage, P., 2008, Noncatalytic gasification of lignin in supercritical water, *Energy and Fuels*, 22:1328–1334 pp.

Roth, L.G., Seager, Lynch F.J., and Weiner, J., 1960, *Structure, Extractives and Utilization of Bark*, Bibliographic series No.191, The Institute of Paper Chemistry, 446 pp.

Sağlam, M., 2010, Investigation of hydrogen and/or methane production from lignocellulosic wet biomass by supercritical water gasification, TUBITAK Project No: 106T748.

Sağlam, M., 2013, Investigation Of The Hemicellulose Behaviour In The Structure Of Plant Biomass By Using Of Model Compounds In Supercritical Water Gasification For Hydrogen And Methane Production. TUBITAK Project No: 109M284.

Saha, B.C., 2003, Hemicellulose Bioconversion, *Journal of Ind Microbiol Biotechnol*, 30:279-91 pp.

Saracoglu, N., 2007, Zero Emission Power Generation Workshop, Gebze, Turkey.

Sharma, D.K., 2006, Bioprospecting for drug, research and functional foods for the prevention of diseases-Role of flavonoids in drug development, *Journal of Scientific & Industrial Research*, 65:391-401 pp.

Sinag, A., Kruse, A., and Schwarzkopf, V., 2003, Key compounds of the hydropyrolysis of glucose in supercritical water in the presence of K_2CO_3 . *Ind Eng Chem Res*, 42:3516–3521 pp.

Sjöström, E., 1981, *Wood Chemistry*, Academic Press, New York.

Sutton, D., Kelleher, B., and Ross, J., 2001, Review of literature on catalysts for biomass gasification, *Fuel Processing Technology*, 73: 155 pp.

REFERENCES (Continued)

- Tang H., and Kitagawa K.,** 2005, Supercritical water gasification of biomass: thermodynamic analysis with direct Gibbs free energy minimization, *Chem Eng J*, 106:261–267 pp.
- Tokarzewska-Zadora, J., Rogalski J., and Szczodrak J.,** 2005, Xylan degrading enzymes characterization and application in biotechnology, *Biotechnologia* 82:69-163 pp.
- Turkyilmaz, O.,** 2013, Turkey Energy Outlook, ICCI, 35 April, Turkey.
- Turner, J.A.,** 2004, Sustainable Hydrogen Production, *Science*, 305:972-974 pp.
- Uematsu, M., and Franck, E.U.,** 1980, Static dielectric constant of water and steam. *Journal of Physical and Chemical Reference Data*, 9: 1291-1306 pp
- Valenzuela, M.B.,** 2006, Batch aqueous-phase reforming of lignocellulosic biomass for hydrogen production, MSc Thesis, Georgia Institute of . Technology, 163 p.
- Vigouroux, R.Z.,** 2001, Pyrolysis of biomass, Royal Institute of Technology, Chemical Technology, Stockholm.
- Wang, D.,** 2003, Wood Chemistry Class, Structure and Properties of Hemicellulose, <http://web.nchu.edu.tw/pweb/users/taiwanfir/lesson/10393.pdf>
- Watanabe, M., Sato, T., Inomata, H., Smith R. L., Jr., Arai, K., and Kruse, A., Dinjus, E.,** 2004, Chemical Reactions of C1 Compounds in Near-Critical and Supercritical Water, *Chem. Rev*, 104:5803-5821 pp.
- Watanabe, M., Aizawa, Y., Iida, T., Levy, C., Aida, TM., and Inomata, H.,** 2005, Glucose reactions within the heating period and the effect of heating rate on the reactions in hot compressed water. *Carbohydrate Research*, 340:1931-1939 pp.
- Weissermehl, K., Jürgen Arge H.,** 1978, Industrial Organic Chemistry, Verlag Chemie, Weinheim, New York.

REFERENCES (Continued)

Williams, P.T., and Onwudili, J., 2005, Composition of products from the supercritical water gasification of glucose: a model biomass compound. *Ind. Eng. Chem. Res.*, 44: 8739–8749 pp.

Williams, P.T., and Onwudili, J., 2006, Subcritical and Supercritical Water Gasification of Cellulose, Starch, Glucose, and Biomass Waste, *Energy&Fuels*, 20:1259-1265 pp.

Wise, E.L., and Jahn, E.C., 1952, *Wood Chemistry*, American Chemical Society, New York.

World Energy Council 2012, Turkey's energy facts and figures, <http://dektmk.org.tr/upresimler/TURKEYSENERGYFACTSANDFIGURES2012.pdf>

World Energy Resources Survey, 2013, published by World Energy Council, http://www.worldenergy.org/wpcontent/uploads/2013/09/Complete_WER_2013_Survey.pdf

Xianghong, Q., Mark, R. N., Mark, D., David, K. J., and Michael, E. H. 2005, Ab initio molecular dynamics simulations of beta-D-glucose and beta-D-xylose degradation mechanisms in acidic aqueous solution. *Carbohydrate Research*, 340:2319–2327 pp.

Xu, X., and Antal, Jr. M .J., 1998, Gasification of Sewage Sludge and Other Biomass for Hydrogen Production in Supercritical Water. *Environmental Progress*, 11: 215-220 pp.

Yanik, J., Ebale, S., Kruse, A., Saglam, M., and Yuksel, M., 2008, Biomass gasification in supercritical water: Part II. Effect of catalyst, *Int J Hydrogen Energy*, 33:4520-4526 pp.

Yong, T.L.K., and Matsumura, Y., 2013, Reaction pathways of phenol and benzene decomposition in supercritical water gasification, *J of the Japan Petroleum Institute*, 56:331-343pp.

REFERENCES (Continued)

Yoshida, T., and Matsumura Y., 2001, Gasification of cellulose, xylan and lignin mixtures in supercritical water, *Ind. Eng. Chem. Res.*, 40:5469-5474 pp.

Yoshida, Y., Dowaki, K., Matsumura, Y., Matsubishi, R., Li, D., and Ishitani, H., 2003, Comprehensive comparison of efficiency and CO₂ emissions between biomass energy conversion technologies—position of supercritical water gasification in biomass technologies, *Biomass Bioenergy*; 25:257–272 pp.

Yu, J., and Savage, P.E., 1998, Decomposition of Formic Acid under Hydrothermal Conditions, *Ind Eng Chem Res*, 37:2-10 pp.

Zhang, L., Champagne, P., Xu, C., 2011, Screening of supported transition metal catalysts for hydrogen production from glucose via catalytic supercritical water gasification, *International Journal of Hydrogen Energy*, 36: 9591-9601 pp.

Zhang, Y., 2010, Hydrothermal Liquefaction to Convert Biomass into Crude Oil, <http://ageweb.age.uiuc.edu/bee/research/IntroHTL.pdf>.

CURRICULUM VITAE

The following papers have been published from the PhD work:

Manuscript ID: UESO-2014-019 – Energy Sources, Part A: Recovery, Utilization, and Environmental Effects.

Title: Characterization of products evolved from supercritical water gasification of xylose (principal sugar in hemicelluloses).

The following papers have been submitted for publication from the PhD work:

Manuscript Number: JBB-D-14-01328 – Biomass and Bioenergy

Title: Hydrothermal gasification of xylose: Effect of reaction temperature, pressure and K_2CO_3 as a catalyst on product distribution.

Manuscript Number: HE-D-14-03412 - International Journal of Hydrogen Energy

Title: Supercritical water gasification of phenol as a model for plant biomass

Oral presented papers in the international Congresses from the PhD work:

IUPAC 2013 - 44th World Chemistry Congress, 11-16 August 2013, İstanbul

“Catalytic Gasification of Xylose In Supercritical Water”

IEESE 2014 - 7th International Ege Energy Symposium & Exhibition, 18-20 June 2014, Uşak-Turkey.

“Supercritical water gasification of phenol as a model for plant biomass”

CRETE 2014 – 4th International Conference on Industrial and Hazardous Waste Management, 2-5 September 2014, Crete-Greece

“Hydrothermal gasification of arabinose as a model compound for plant biomass waste”

APPENDICES

Tables 1-43: Experimental results for SCWG of the model compounds at different temperatures, pressures, and catalysts.

Table 1. Experimental results for SCWG of Xylose at different temperatures and catalyst.

Experiment No	1	2	3	4	5	6	7	8
Reaction Temperature, °C	300	400	500	600	300	400	500	600
Reaction Pressure, atm	80	245	360	440	80	250	345	430
Catalyst, 10 wt. %	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Gas Composition, % mol								
CH ₄	0.8	4.9	17.8	25.1	1.1	5.5	18.8	22.8
H ₂	13.5	15.5	26.8	28.9	11.2	21.0	28.6	36.6
CO ₂	78.0	72.7	47.5	40.9	79.3	68.5	45.4	36.9
CO	7.2	3.6	1.5	0.6	8.1	1.8	0.6	0.2
C ₂ -C ₄	0.5	3.3	6.4	4.5	0.3	3.2	6.6	3.5
Gas Product, mol/ kg Xylose								
CH ₄	0.1	0.5	3.4	7.1	0.1	0.8	4.6	9.0
H ₂	0.8	1.6	5.4	8.2	1.1	3.0	6.9	14.4
CO ₂	5.4	7.6	9.5	11.6	7.8	10.1	11.0	14.3
CO	0.5	0.4	0.3	0.17	0.8	0.3	0.2	0.1
C ₂ -C ₄	0.1	0.3	1.3	1.5	0.03	0.5	1.6	1.4
Gas Product, g/kg Xylose								
Gas Product Yield, wt. %	18.5	28.6	44.2	67.0	26.6	37.1	60.5	81.9
Aqueous Product Yield, wt. %	29.1	28.7	23.9	9.3	36.1	32.7	18.0	6.8
Solid Product Yield (Coke+Tar), wt. %	51.0	40.8	27.9	19.6	34.0	28.6	20.4	10.7
TOC of Aqueous Product, mg/L	1370.0	1350.0	1106.0	435.0	1700.0	1550.0	850.0	320.0
Amount of Coke, g/kg Xylose	250.0	200.0	133.3	95.8	200.0	141.6	103.1	52.5

Table 2. Experimental results for SCWG of Xylose at different temperatures and catalysts.

Experiment No	9	10	11	12	13	14	15	16
Reaction Temperature, °C	300	400	500	600	300	400	500	600
Reaction Pressure, atm	90	250	340	440	80	260	340	440
Catalyst, 10 wt. %	KOH	KOH	KOH	KOH	AC-Ni	AC-Ni	AC-Ni	AC-Ni
Gas Composition, % mol								
CH₄	0.9	7.3	17.9	21.4	0.6	5.7	18.3	27.9
H₂	13.7	25.5	28.3	33.6	13.3	18.9	25.6	33.6
CO₂	80.5	63.1	48.2	40.6	79.4	68.1	48.8	33.7
CO	4.5	1.2	0.4	0.2	5.9	4.1	0.8	0.3
C₂-C₄	0.4	2.9	5.2	4.2	0.8	3.2	6.5	4.5
Gas Product, mol/ kg Xylose								
CH₄	0.1	1.3	6.7	8.1	0.1	0.8	4.1	9.9
H₂	1.3	4.2	7.8	12.8	1.2	2.7	5.7	11.9
CO₂	7.6	10.5	13.3	15.3	7.3	9.6	10.8	11.9
CO	0.4	0.2	0.1	0.1	0.5	0.4	0.2	0.1
C₂-C₄	0.03	0.5	1.4	1.6	0.1	0.5	1.4	1.6
Gas Product, g/kg Xylose								
Gas Product Yield, wt. %	25.0	40.1	66.2	83.9	24.8	36.9	57.3	79.5
Aqueous Product Yield, wt. %	29.9	24.4	14.9	4.2	28.1	23.2	18.0	3.5
Solid Product Yield (Coke+Tar), wt. %	42.1	32.0	16.8	10.1	43.5	36.5	21.2	11.9
TOC of Aqueous Product, mg/L	1420.0	1160.0	710.0	198.0	1320.0	1090.0	850.0	165.0
Amount of Coke, g/kg Xylose	208.3	158.3	83.3	50.2	213.3	179.2	104.2	58.3

Table 3. Experimental results for SCWG of Xylose at different temperatures and catalysts.

Experiment No	17	18	19	20				
Reaction Temperature, °C	300	400	500	600				
Reaction Pressure, atm	90	240	325	450				
Catalyst, 10 wt. %	AC-Ru	AC-Ru	AC-Ru	AC-Ru				
Gas Composition, % mol								
CH₄	1.3	7.7	16.5	17.2				
H₂	14.3	35.8	38.8	39.5				
CO₂	79.5	51.5	39.2	39.1				
CO	4.4	2.3	1.3	0.4				
C₂-C₄	0.5	2.7	4.2	3.8				
Gas Product, mol/ kg Xylose								
CH₄	0.1	1.3	4.4	6.8				
H₂	1.3	5.8	9.5	15.5				
CO₂	7.5	8.6	10.4	15.4				
CO	0.5	0.4	0.3	0.1				
C₂-C₄	0.1	0.4	1.1	1.5				
Gas Product, g/kg Xylose	345.9	431.1	651.1	876.9				
Gas Product Yield, wt. %	24.4	34.1	57.4	79.6				
Aqueous Product Yield, wt. %	33.1	31.9	20.8	4.3				
Solid Product Yield (Coke+Tar), wt. %	38.2	29.7	19.5	12.7				
TOC of Aqueous Product, mg/L	1560.0	1500.0	980.0	205.0				
Amount of Coke, g/kg Xylose	187.6	145.8	95.8	66.7				

Table 4. Experimental results for SCWG of Arabinose at different temperatures and catalyst.

Experiment No	21	22	23	24	25	26	27	28
Reaction Temperature, °C	300	400	500	600	300	400	500	600
Reaction Pressure, atm	80	245	350	440	100	260	370	440
Catalyst, 10 wt. %	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Gas Composition, % mol								
CH ₄	0.9	3.8	18.8	27.2	1.3	7.7	20.2	20.6
H ₂	15.6	21.5	26.5	28.8	12.7	21.6	29.5	37.6
CO ₂	75.6	66.9	47.5	38.9	78.8	64.4	43.3	38.9
CO	7.2	4.8	0.6	0.3	6.7	2.8	0.4	0.2
C ₂ -C ₄	0.7	3.0	6.6	4.8	0.5	3.5	6.6	2.7
Gas Product, mol/ kg Arabinose								
CH ₄	0.06	0.4	3.5	7.6	0.1	1.2	5.0	8.6
H ₂	1.0	2.1	5.0	8.1	1.5	3.2	7.3	15.7
CO ₂	4.7	6.5	8.9	10.9	9.1	9.5	10.7	16.2
CO	0.5	0.4	0.1	0.08	0.8	0.6	0.1	0.1
C ₂ -C ₄	0.05	0.3	1.2	1.3	0.05	0.5	1.6	1.1
Gas Product, g/kg Arabinose								
Gas Product	222.6	318.9	511.7	674.3	355.4	489.8	631.2	927.1
Gas Product Yield, wt. %	16.1	24.4	47.4	66.7	25.4	37.9	60.1	83.8
Aqueous Product Yield, wt. %	34.7	28.4	23.2	9.1	35.8	32.0	15.8	3.5
Solid Product Yield (Coke+Tar), wt. %	47.1	43.8	25.2	20.2	35.3	26.1	20.2	10.1
TOC of Aqueous Product, mg/L	1650.0	1350.0	1100.0	435.0	1710.0	1520.0	750.0	165.0
Amount of Coke, g/kg Arabinose	233.4	216.7	125.0	100.0	175.1	129.1	100.0	50.1

Table 5. Experimental results for SCWG of Arabinose at different temperatures and catalyst.

Experiment No	29	30	31	32	33	34	35	36
Reaction Temperature, °C	300	400	500	600	300	400	500	600
Reaction Pressure, atm	100	235	340	480	95	260	350	445
Catalyst, 10 wt. %	KOH	KOH	KOH	KOH	AC-Ni	AC-Ni	AC-Ni	AC-Ni
Gas Composition, % mol								
CH ₄	1.1	6.7	20.7	22.4	0.8	4.7	17.4	25.7
H ₂	8.6	24.3	30.7	36.9	15.1	20.2	27.7	29.3
CO ₂	78.4	63.3	42.7	37.3	77.3	69.4	47.1	38.9
CO	11.5	2.6	0.3	0.2	5.9	2.7	1.4	0.3
C ₂ -C ₄	0.4	3.1	5.6	3.2	0.9	3.0	6.4	5.8
Gas Product, mol/ kg Arabinose								
CH ₄	0.1	1.1	5.1	9.2	0.06	0.6	3.7	8.4
H ₂	0.8	3.9	7.5	15.2	1.3	2.7	6.0	9.5
CO ₂	7.6	10.1	10.5	15.4	6.4	9.1	10.1	12.7
CO	1.1	0.4	0.1	0.1	0.5	0.4	0.3	0.1
C ₂ -C ₄	0.03	0.1	1.4	1.3	0.08	0.4	1.4	1.9
Gas Product, g/kg Arabinose	369.6	485.2	659.2	912.1	302.7	440.7	581.1	768.1
Gas Product Yield, wt. %	27.1	36.1	58.0	85.0	21.8	33.7	53.4	78.4
Aqueous Product Yield, wt. %	37.9	32.8	15.8	4.6	41.7	36.2	20.2	5.5
Solid Product Yield (Coke+Tar), wt. %	32.0	26.9	22.7	8.4	32.8	25.2	23.2	14.3
TOC of Aqueous Product, mg/L	1800.0	1560.0	750.0	220.0	1980.0	1720.0	960.0	270.0
Amount of Coke, g/kg Arabinose	158.3	133.3	112.5	41.6	162.5	125.0	115.0	70.8

Table 6. Experimental results for SCWG of Arabinose at different temperatures and catalyst.

Experiment No	37	38	39	40				
Reaction Temperature, °C	300	400	500	600				
Reaction Pressure, atm	90	245	356	443				
Catalyst, 10 wt. %	AC-Ru	AC-Ru	AC-Ru	AC-Ru				
Gas Composition, % mol								
CH₄	1.4	5.7	19.8	20.2				
H₂	17.5	30.8	32.7	34.5				
CO₂	76.1	57.8	43.0	40.6				
CO	4.2	2.8	0.8	0.5				
C₂-C₄	0.8	2.9	3.7	4.2				
Gas Product, mol/ kg Arabinose								
CH₄	0.1	0.8	5.0	7.2				
H₂	1.5	4.2	8.2	12.4				
CO₂	6.6	8.0	10.8	14.5				
CO	0.4	0.3	0.2	0.2				
C₂-C₄	0.07	0.4	0.9	1.5				
Gas Product, g/kg Arabinose	308.0	402.2	615.3	819.0				
Gas Product Yield, wt. %	22.0	38.7	55.6	77.8				
Aqueous Product Yield, wt. %	38.9	29.9	18.4	3.3				
Solid Product Yield (Coke+Tar), wt. %	34.5	27.8	21.4	16.8				
TOC of Aqueous Product, mg/L	1850.0	1420.0	875.0	155.0				
Amount of Coke, g/kg Arabinose	170.8	137.5	105.8	83.3				

Table 7. Experimental results for SCWG of Tannic acid at different temperatures and catalyst.

Experiment No	41	42	43	44	45	46
Reaction Temperature, °C	400	500	600	400	500	600
Reaction Pressure, atm	230	365	430	270	340	440
Catalyst, 10 wt. %	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Gas Composition, % mol						
CH ₄	1.5	11.3	19.4	5.9	13.5	19.2
H ₂	12.4	22.2	25.0	19.5	27.4	36.5
CO ₂	76.7	59.2	50.6	71.5	54.8	40.6
CO	7.6	0.6	0.2	0.3	0.2	0.1
C ₂ -C ₄	1.8	6.7	4.8	2.8	4.1	3.6
Gas Product, mol/ kg Tannic acid						
CH ₄	0.3	2.7	7.5	1.5	4.8	10.1
H ₂	1.9	5.3	8.9	5.1	9.8	19.1
CO ₂	11.9	14.0	18.2	18.6	19.6	21.3
CO	1.2	0.14	0.07	0.08	0.07	0.05
C ₂ -C ₄	0.3	1.6	1.7	0.7	1.5	1.9
Gas Product, g/kg Tannic acid	577.8	737.7	1008.6	882.8	1020.8	1214.4
Gas Product Yield, wt. %	31.3	46.8	66.5	49.7	63.4	81.2
Aqueous Product Yield, wt. %	32.7	24.5	11.3	20.3	13.2	8.7
Solid Product Yield (Coke+Tar), wt. %	33.4	26.2	18.4	26.7	20.2	9.1
TOC of Aqueous Product, mg/L	1745.0	1310.0	605.0	1085.0	705.0	465.0
Amount of Coke, g/kg Tannic acid	210.1	175.2	123.2	178.2	135.2	65.1

Table 8. Experimental results for SCWG of Tannic acid at different temperatures and catalysts.

Experiment No	47	48	49	50	51	52
Reaction Temperature, °C	400	500	600	400	500	600
Reaction Pressure, atm	245	335	445	250	370	435
Catalyst, 10 wt. %	KOH	KOH	KOH	AC-Ni	AC-Ni	AC-Ni
Gas Composition, % mol						
CH ₄	3.80	12.9	18.8	2.1	11.7	18.3
H ₂	20.2	29.4	39.3	15.1	20.7	26.1
CO ₂	73.2	53.2	39.1	77.8	60.6	52.1
CO	0.7	0.4	0.2	3.2	0.5	0.3
C ₂ -C ₄	2.1	4.1	2.6	1.8	6.5	3.2
Gas Product, mol/ kg Tannic acid						
CH ₄	1.0	4.6	10.5	0.5	3.7	8.1
H ₂	5.2	10.7	21.8	3.6	6.6	11.7
CO ₂	18.8	19.4	21.7	18.8	19.2	23.2
CO	0.17	0.14	0.1	0.8	0.16	0.12
C ₂ -C ₄	0.5	1.5	1.4	0.4	2.0	1.4
Gas Product, g/kg Tannic acid						
Gas Product Yield, wt. %	48.0	62.7	80.8	47.6	63.3	79.5
Aqueous Product Yield, wt. %	19.1	11.8	8.8	21.5	13.4	8.9
Solid Product Yield (Coke+Tar), wt. %	29.2	22.3	9.8	28.8	21.7	11.1
TOC of Aqueous Product, mg/L	1020.0	630.0	471.0	1150.0	715.0	476.0
Amount of Coke, g/kg Tannic acid	195.2	158.1	71.5	204.9	155.1	79.4

Table 9. Experimental results for SCWG of Tannic acid at different temperatures and catalyst.

Experiment No	53	54	55				
Reaction Temperature, °C	400	500	600				
Reaction Pressure, atm	252	355	445				
Catalyst, 10 wt. %	AC-Ru	AC-Ru	AC-Ru				
Gas Composition, % mol							
CH₄	2.0	16.7	18.1				
H₂	17.4	32.6	37.9				
CO₂	77.0	47.0	41.1				
CO	2.4	1.2	0.8				
C₂-C₄	1.2	2.5	2.1				
Gas Product, mol/ kg Tannic acid							
CH₄	0.5	6.8	10.0				
H₂	4.3	13.3	21.0				
CO₂	19.0	19.1	22.6				
CO	0.6	0.5	0.4				
C₂-C₄	0.3	1.0	1.1				
Gas Product, g/kg Tannic acid	881.4	1029.8	1251.6				
Gas Product Yield, wt. %	47.1	65.2	81.1				
Aqueous Product Yield, wt. %	20.3	11.6	8.7				
Solid Product Yield (Coke+Tar), wt. %	30.2	21.2	8.4				
TOC of Aqueous Product, mg/L	1085.0	618.0	465.0				
Amount of Coke, g/kg Tannic acid	215.6	151.2	60.6				

Table 10. Experimental results of Gallic acid SCWG at 400°C, 500°C and 600°C without and with K₂CO₃.

Experiment No	56	57	58	59	60	61
Reaction Temperature, °C	400	500	600	400	500	600
Reaction Pressure, atm	225	360	420	275	340	440
Catalyst, 10 wt. %	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Gas Composition, % mol						
CH ₄	1.8	10.6	21.2	3.6	12.9	19.9
H ₂	14.4	21.8	24.2	17.2	29.4	37.1
CO ₂	80.8	61.6	49.2	76.0	52.3	39.4
CO	0.8	0.3	0.1	0.4	0.3	0.2
C ₂ -C ₄	2.2	5.7	5.3	2.8	5.1	5.0
Gas Product, mol/ kg Gallic acid						
CH ₄	0.3	2.3	7.3	0.9	4.2	9.4
H ₂	2.1	4.7	8.3	4.2	9.6	17.5
CO ₂	11.8	13.1	16.9	18.8	17.1	18.6
CO	0.1	0.05	0.03	0.1	0.08	0.06
C ₂ -C ₄	0.3	1.2	1.9	0.7	1.7	2.4
Gas Product, g/kg Gallic acid	543.0	672.0	953.8	880.8	909.3	1101.5
Gas Product Yield, wt. %	32.4	44.9	69.9	51.9	62.2	82.7
Aqueous Product Yield, wt. %	36.7	30.1	13.0	22.2	17.2	6.2
Solid Product Yield (Coke+Tar), wt. %	27.8	22.3	13.8	22.6	17.3	9.2
TOC of Aqueous Product, mg/L	1950.0	1600.0	690.0	1180.0	914.0	330.0
Amount of Coke, g/kg Gallic acid	167.6	137.8	88.5	139.6	107.0	65.2

Table 11. Experimental results of Gallic acid SCWG at 400°C, 500°C and 600°C with KOH.

Experiment No	62	63	64
Reaction Temperature, °C	400	500	600
Reaction Pressure, atm	240	370	440
Catalyst, 10 wt. %	KOH	KOH	KOH
Gas Composition, % mol			
CH ₄	3.6	14.2	20.4
H ₂	16.5	29.9	36.5
CO ₂	75.6	50.7	38.1
CO	0.4	0.2	0.1
C ₂ -C ₄	3.9	5.0	4.9
Gas Product, mol/ kg Gallic acid			
CH ₄	0.9	4.6	9.7
H ₂	4.0	9.6	17.4
CO ₂	19.1	16.3	18.1
CO	0.1	0.06	0.04
C ₂ -C ₄	1.0	1.6	2.4
Gas Product, g/kg Gallic acid	905.6	875.7	1083.5
Gas Product Yield, wt. %	54.5	60.6	81.9
Aqueous Product Yield, wt. %	21.8	16.5	6.5
Solid Product Yield (Coke+Tar), wt. %	22.3	19.6	9.8
TOC of Aqueous Product, mg/L	1157.0	876.0	345.0
Amount of Coke, g/kg Gallic acid	148.9	121.0	69.8

Table 12. Experimental results of Phloroglucinol SCWG at 400°C, 500°C and 600°C without and with K₂CO₃.

Experiment No	65	66	67	68	69	70
Reaction Temperature, °C	400	500	600	400	500	600
Reaction Pressure, atm	240	360	410	220	340	470
Catalyst, 10 wt. %	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Gas Composition, % mol						
CH₄	3.4	31.5	41.4	9.8	32.6	38.1
H₂	2.6	9.0	11.3	4.5	19.5	24.3
CO₂	91.4	57.6	45.7	84.2	45.8	35.1
CO	1.6	0.8	0.4	1.0	0.6	0.4
C₂-C₄	1.0	1.1	1.2	0.5	1.5	2.1
Gas Product, mol/ kg Phloroglucinol						
CH₄	0.6	9.0	17.9	2.1	11.6	20.6
H₂	0.4	2.6	4.1	1.0	6.9	13.4
CO₂	15.6	16.5	19.4	18.4	16.3	17.4
CO	0.3	0.2	0.2	0.3	0.25	0.2
C₂-C₄	0.2	0.3	0.5	0.1	0.5	1.1
Gas Product, g/kg Phloroglucinol	713.2	892.8	1173.8	857.6	943.6	1171.6
Gas Product Yield, wt. %	35.5	55.8	80.1	44.4	61.7	89.7
Aqueous Product Yield, wt. %	45.4	29.0	8.8	41.9	28.5	6.7
Solid Product Yield (Coke+Tar), wt. %	15.4	12.2	10.0	10.6	6.9	3.0
TOC of Aqueous Product, mg/L	2375.0	1515.0	425.0	2190.0	1495.0	355.0
Amount of Coke, g/kg Phloroglucinol	109.3	87.4	71.6	65.5	43.7	21.8

Table 13. Experimental results of Phloroglucinol SCWG at 400°C, 500°C and 600°C with KOH.

Experiment No	71	72	73
Reaction Temperature, °C	400	500	600
Reaction Pressure, atm	215	365	460
Catalyst, 10 wt. %	KOH	KOH	KOH
Gas Composition, % mol			
CH₄	12.8	32.5	37.4
H₂	3.8	15.4	23.6
CO₂	81.8	50.6	36.5
CO	1.2	0.7	0.3
C₂-C₄	0.4	0.8	2.2
Gas Product, mol/ kg Phloroglucinol			
CH₄	2.8	11.1	19.7
H₂	0.8	5.3	12.4
CO₂	17.7	17.3	19.2
CO	0.25	0.2	0.15
C₂-C₄	0.09	0.27	1.1
Gas Product, g/kg Phloroglucinol	835.8	976.4	1233.0
Gas Product Yield, wt. %	43.9	61.6	88.1
Aqueous Product Yield, wt. %	41.3	27.2	5.4
Solid Product Yield (Coke+Tar), wt. %	12.0	8.3	3.4
TOC of Aqueous Product, mg/L	2160.0	1423.0	280.0
Amount of Coke, g/kg Phloroglucinol	87.4	54.6	21.9

Table 14. Experimental results of Pyrogallol SCWG at 400°C, 500°C and 600°C without and with K₂CO₃.

Experiment No	74	75	76	77	78	79
Reaction Temperature, °C	400	500	600	400	500	600
Reaction Pressure, atm	245	360	420	240	350	425
Catalyst, 10 wt. %	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Gas Composition, % mol						
CH ₄	1.7	9.8	17.5	5.4	17.7	19.8
H ₂	9.0	19.3	25.2	17.6	30.9	40.1
CO ₂	72.6	60.4	50.1	71.5	45.0	37.3
CO	13.9	1.5	0.2	1.0	0.6	0.2
C ₂ -C ₄	2.8	9.0	7.0	4.5	5.8	2.6
Gas Product, mol/ kg Pyrogallol						
CH ₄	0.2	1.9	6.0	1.0	5.9	12.1
H ₂	1.3	3.7	8.6	3.4	10.0	24.5
CO ₂	10.2	11.6	17.1	13.7	14.7	22.8
CO	2.0	0.3	0.07	0.2	0.2	0.1
C ₂ -C ₄	0.4	1.7	2.4	0.9	1.9	1.6
Gas Product, g/kg Pyrogallol	526.6	624.4	963.6	667.2	841.2	1312.6
Gas Product Yield, wt. %	28.0	38.1	61.4	35.8	53.2	82.0
Aqueous Product Yield, wt. %	40.9	31.3	16.2	36.9	26.1	4.5
Solid Product Yield (Coke+Tar), wt. %	29.8	28.0	19.3	25.0	17.2	10.7
TOC of Aqueous Product, mg/L	2750.0	2100.0	1090.0	2480.0	1755.0	303.0
Amount of Coke, g/kg Pyrogallol	221.1	199.8	148.8	178.5	123.2	76.5

Table 15. Experimental results of Pyrogallol SCWG at 400°C, 500°C and 600°C with KOH.

Experiment No	80	81	82
Reaction Temperature, °C	400	500	600
Reaction Pressure, atm	220	360	450
Catalyst, 10 wt. %	KOH	KOH	KOH
Gas Composition, % mol			
CH₄	5.5	17.5	19.4
H₂	19.4	34.5	42.4
CO₂	69.5	42.2	35.9
CO	0.8	0.5	0.3
C₂-C₄	4.8	5.3	2.0
Gas Product, mol/ kg Pyrogallol			
CH₄	1.0	5.8	12.0
H₂	3.6	11.5	26.2
CO₂	13.0	14.1	20.7
CO	0.1	0.2	0.18
C₂-C₄	0.9	1.8	1.2
Gas Product, g/kg Pyrogallol	634.0	813.8	1208.2
Gas Product Yield, wt. %	34.6	51.7	78.5
Aqueous Product Yield, wt. %	39.4	25.0	6.1
Solid Product Yield (Coke+Tar), wt. %	22.2	19.8	11.7
TOC of Aqueous Product, mg/L	2680.0	1680.0	408.0
Amount of Coke, g/kg Pyrogallol	183.1	136.1	89.2

Table 16. Experimental results of Pectin SCWG at 400°C, 500°C and 600°C without and with K₂CO₃.

Experiment No	83	84	85	86	87	88
Reaction Temperature, °C	400	500	600	400	500	600
Reaction Pressure, atm	235	350	425	230	340	430
Catalyst, 10 wt. %	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Gas Composition, % mol						
CH ₄	2.7	14.1	12.8	3.8	12.2	20.1
H ₂	14.6	26.6	32.9	25.2	34.9	42.7
CO ₂	79.1	55.1	52.0	68.4	48.6	34.5
CO	1.2	0.6	0.2	1.0	0.4	0.1
C ₂ -C ₄	2.4	3.6	2.1	1.6	3.9	2.6
Gas Product, mol/ kg Pectin						
CH ₄	0.3	2.7	3.7	0.6	3.2	8.2
H ₂	1.5	7.4	9.4	4.0	9.4	17.5
CO ₂	8.4	10.5	14.8	10.8	13.1	14.1
CO	0.1	0.1	0.05	0.16	0.09	0.04
C ₂ -C ₄	0.3	0.7	0.6	0.25	1.0	1.1
Gas Product, g/kg Pectin	392.2	550.8	754.6	507.3	688.9	832.1
Gas Product Yield, wt. %	30.5	48.8	64.5	39.6	62.1	81.5
Aqueous Product Yield, wt. %	26.1	16.3	12.4	22.1	15.8	6.6
Solid Product Yield (Coke+Tar), wt. %	39.6	32.1	20.4	33.3	19.8	11.0
TOC of Aqueous Product, mg/L	1155	725	550	980	700	295
Amount of Coke, g/kg Pectin	183.2	151.3	100.1	158.1	91.6	58.3

Table 17. Experimental results of Pectin SCWG at 400°C, 500°C and 600°C with KOH.

Experiment No	89	90	91
Reaction Temperature, °C	400	500	600
Reaction Pressure, atm	225	355	460
Catalyst, 10 wt. %	KOH	KOH	KOH
Gas Composition, % mol			
CH ₄	3.7	12.8	18.7
H ₂	24.2	37.9	42.5
CO ₂	69.4	44.9	36.2
CO	1.1	0.5	0.2
C ₂ -C ₄	1.6	3.9	2.4
Gas Product, mol/ kg Pectin			
CH ₄	0.6	2.7	7.7
H ₂	3.7	7.9	17.3
CO ₂	10.7	9.4	14.8
CO	0.16	0.1	0.08
C ₂ -C ₄	0.24	0.8	0.9
Gas Product, g/kg Pectin	501.9	507.4	847.2
Gas Product Yield, wt. %	39.2	60.6	80.7
Aqueous Product Yield, wt. %	25.3	15.3	4.7
Solid Product Yield (Coke+Tar), wt. %	33.0	21.3	10.8
TOC of Aqueous Product, mg/L	1125	680	210
Amount of Coke, g/kg Pectin	158.2	100.0	50.0

Table 18. Experimental results of Galacturonic acid SCWG at 400°C, 500°C and 600°C without and with K₂CO₃.

Experiment No	92	93	94	95	96	97
Reaction Temperature, °C	400	500	600	400	500	600
Reaction Pressure, atm	235	350	425	230	340	430
Catalyst, 10 wt. %	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Gas Composition, % mol						
CH ₄	4.8	11.1	16.4	5.5	15.5	18.5
H ₂	22.6	23.1	28.7	22.9	28.0	35.8
CO ₂	70.0	62.3	52.1	69.1	51.9	43.3
CO	1.0	0.3	0.2	1.2	0.4	0.3
C ₂ -C ₄	1.6	3.2	2.6	1.3	4.2	2.1
Gas Product, mol/ kg Pectin						
CH ₄	0.7	1.9	4.3	0.9	3.8	6.9
H ₂	3.1	3.9	7.4	4.0	6.8	13.4
CO ₂	9.6	10.4	13.5	11.6	12.6	16.2
CO	0.1	0.05	0.05	0.2	0.1	0.1
C ₂ -C ₄	0.2	0.5	0.7	0.2	1.0	0.8
Gas Product, g/kg Pectin	448.6	512.52	700.0	544.4	661.6	876.8
Gas Product Yield, wt. %	35.1	44.3	63.1	41.6	61.6	81.5
Aqueous Product Yield, wt. %	17.8	16.1	9.7	19.3	13.6	5.8
Solid Product Yield (Coke+Tar), wt. %	43.3	35.2	25.3	35.1	19.8	10.8
TOC of Aqueous Product, mg/L	690	625	370	750	510	225
Amount of Coke, g/kg Pectin	201.1	186.7	134.1	162.8	105.3	57.4

Table 19. Experimental results of Galacturonic acid SCWG at 400°C, 500°C and 600°C with KOH.

Experiment No	98	99	100
Reaction Temperature, °C	400	500	600
Reaction Pressure, atm	225	355	460
Catalyst, 10 wt. %	KOH	KOH	KOH
Gas Composition, % mol			
CH₄	3.2	14.3	17.3
H₂	19.8	30.5	40.3
CO₂	74.3	51.0	39.9
CO	1.1	0.6	0.3
C₂-C₄	1.6	3.6	2.2
Gas Product, mol/ kg Pectin			
CH₄	0.5	3.9	7.1
H₂	3.0	8.2	16.3
CO₂	11.1	13.7	16.1
CO	0.2	0.2	0.1
C₂-C₄	0.2	1.0	0.9
Gas Product, g/kg Pectin	514.0	717.2	884.8
Gas Product Yield, wt. %	39.9	65.2	82.1
Aqueous Product Yield, wt. %	20.4	13.5	2.8
Solid Product Yield (Coke+Tar), wt. %	37.1	19.3	12.6
TOC of Aqueous Product, mg/L	790	524	110
Amount of Coke, g/kg Pectin	172.4	95.7	62.2

Table 20. Experimental results of Xylose SCWG at 400°C for the pressures 200, 275, 350, 425 atm without and with K₂CO₃.

Experiment No	101	102	103	104	105	106	107	108
Reaction Temperature, °C	400	400	400	400	400	400	400	400
Reaction Pressure, atm	205	280	350	423	200	275	345	419
Xylose/Water	0.9/11.25	1.6/20	2.6/32.5	3.5/43.75	0.9/11.25	1.6/20	2.6/32.5	3.5/43.75
Catalyst, 10 wt. %	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Gas Composition, % mol								
CH ₄	3.2	5.3	7.1	9.4	3.2	5.4	7.7	10.2
H ₂	22.3	17.5	17.2	18.0	22.4	21.4	20.8	20.3
CO ₂	63.1	68.1	65.7	62.3	70.4	68.6	66.3	63.8
CO	9.1	5.2	4.5	2.5	1.8	1.7	1.3	0.5
C ₂ -C ₄	2.3	3.9	5.5	7.8	2.2	2.9	3.9	5.2
Gas Product, mol/ kg Xylose								
CH ₄	0.4	0.6	0.7	0.8	0.5	0.8	1.1	1.2
H ₂	2.6	1.8	1.6	1.5	3.5	3.0	2.7	2.3
CO ₂	7.8	7.1	6.1	5.3	11.0	9.8	8.7	7.3
CO	1.0	0.6	0.4	0.3	0.3	0.2	0.1	0.05
C ₂ -C ₄	0.3	0.4	0.6	0.7	0.3	0.4	0.6	0.7
Gas Product, g/kg Xylose								
Gas Product Yield, wt. %	30.4	27.9	25.6	24.4	38.7	36.4	34.4	30.0
Aqueous Product Yield, wt. %	28.7	30.8	32.3	33.4	28.2	29.7	33.1	33.7
Solid Product Yield (Coke+Tar), wt. %	36.5	39.1	40.8	41.6	28.9	29.7	30.6	31.8
TOC of Aqueous Product, mg/L	1350	1450	1520	1570	1325	1500	1560	1585
Amount of Coke, g/kg Xylose	175.1	191.8	200.1	204.3	141.7	145.8	151.2	155.8

Table 21. Experimental results of Xylose SCWG at 500°C for the pressures 200, 275, 350, 425 atm without and with K₂CO₃.

Experiment No	109	110	111	112	113	114	115	116
Reaction Temperature, °C	500	500	500	500	500	500	500	500
Reaction Pressure, atm	205	275	355	430	195	275	355	435
Xylose/Water	0.65/8.1	0.9/11.25	1.2/15	1.6/20	0.65/8.1	0.9/11.25	1.2/15	1.6/20
Catalyst, 10 wt. %	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Gas Composition, % mol								
CH ₄	13.4	14.9	18.4	19.6	14.0	15.6	18.8	21.8
H ₂	35.1	31.3	27.7	26.9	35.3	33.5	28.2	28.5
CO ₂	46.2	47.1	47.4	47.8	46.1	46.0	46.6	43.0
CO	1.9	1.6	1.3	0.5	1.0	0.7	0.6	0.3
C ₂ -C ₄	3.4	4.5	5.2	6.2	3.6	4.2	5.8	6.4
Gas Product, mol/ kg Xylose								
CH ₄	3.1	3.2	3.3	3.5	4.2	4.4	4.7	5.1
H ₂	8.2	6.4	5.3	4.8	10.7	9.4	7.0	6.7
CO ₂	10.8	9.7	9.1	8.4	14.4	12.9	11.6	10.2
CO	0.4	0.3	0.2	0.08	0.3	0.2	0.15	0.07
C ₂ -C ₄	0.7	0.9	1.0	1.1	1.1	1.2	1.4	1.5
Gas Product, g/kg Xylose								
Gas Product Yield, wt. %	50.1	49.1	46.8	45.3	65.7	62.6	61.6	58.6
Aqueous Product Yield, wt. %	19.8	20.6	21.4	22.1	15.7	16.2	17.1	17.5
Solid Product Yield (Coke+Tar), wt. %	25.5	27.2	28.9	30.6	14.0	16.3	18.7	21.2
TOC of Aqueous Product, mg/L	930	970	1010	1040	740	760	805	825
Amount of Coke, g/kg Xylose	125.1	133.4	141.8	150.1	68.3	79.1	91.6	104.2

Table22. Experimental results of Xylose SCWG at 600°C for the pressures 200, 275, 350, 425 atm without and with K₂CO₃.

Experiment No	117	118	119	120	121	122	123	124
Reaction Temperature, °C	600	600	600	600	600	600	600	600
Reaction Pressure, atm	195	275	360	420	210	277	345	417
Xylose/Water	0.55/6.9	0.8/10.0	0.9/11.25	1.1/13.75	0.55/6.9	0.8/10.0	0.9/11.25	1.1/13.75
Catalyst, 10 wt. %	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Gas Composition, % mol								
CH ₄	15.8	19.1	22.5	25.3	15.9	17.6	19.5	22.5
H ₂	42.1	38.4	33.7	30.6	41.1	40.0	38.8	36.3
CO ₂	39.2	38.8	39.2	38.3	40.7	39.8	38.7	37.4
CO	1.2	1.0	0.8	0.6	0.7	0.4	0.3	0.2
C ₂ -C ₄	1.7	2.7	3.8	5.2	1.6	2.2	2.7	3.6
Gas Product, mol/ kg Xylose								
CH ₄	5.9	6.4	6.8	7.1	7.3	7.7	8.1	8.6
H ₂	15.7	13.0	10.2	8.5	18.8	17.5	16.1	13.9
CO ₂	14.7	13.1	11.9	10.6	18.6	17.4	16.1	14.3
CO	0.4	0.3	0.2	0.15	0.3	0.2	0.1	0.07
C ₂ -C ₄	0.6	1.0	1.1	1.4	0.7	1.0	1.1	1.4
Gas Product, g/kg Xylose								
Gas Product Yield, wt. %	69.4	68.0	66.6	65.9	86.0	84.7	83.2	80.9
Aqueous Product Yield, wt. %	7.2	8.5	9.1	9.6	5.4	5.8	6.1	6.5
Solid Product Yield (Coke+Tar), wt. %	17.0	18.7	20.2	22.1	5.1	6.8	8.1	9.4
TOC of Aqueous Product, mg/L	340	400	430	450	255	275	290	305
Amount of Coke, g/kg Xylose	83.4	91.7	100.1	108.4	25.1	33.3	40.0	45.8

Table 23. Experimental results of Arabinose SCWG at 400°C for the pressures 200, 275, 350, 425 atm without and with K₂CO₃.

Experiment No	125	126	127	128	129	130	131	132
Reaction Temperature, °C	400	400	400	400	400	400	400	400
Reaction Pressure, atm	205	270	345	410	205	280	340	415
Arabinose/Water	0.9/11.25	1.6/20.0	2.6/32.5	3.5/43.75	0.9/11.25	1.6/20.0	2.6/32.5	3.5/43.75
Catalyst, 10 wt. %	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Gas Composition, % mol								
CH ₄	4.6	7.1	8.6	10.7	5.8	7.2	9.8	11.6
H ₂	19.9	17.7	17.5	16.9	24.2	22.8	20.8	18.8
CO ₂	67.9	66.9	67.4	65.4	66.0	65.5	64.4	62.6
CO	4.5	4.2	1.6	1.5	1.7	1.6	1.4	0.8
C ₂ -C ₄	3.1	4.1	4.9	5.6	2.3	2.9	3.6	6.2
Gas Product, mol/ kg Arabinose								
CH ₄	0.4	0.6	0.7	0.8	1.0	1.2	1.3	1.6
H ₂	1.9	1.5	1.3	1.2	4.0	3.6	2.5	2.4
CO ₂	6.4	5.8	5.1	4.7	11.0	10.1	7.8	7.7
CO	0.4	0.35	0.1	0.1	0.3	0.25	0.15	0.10
C ₂ -C ₄	0.3	0.35	0.37	0.4	0.38	0.45	0.5	0.8
Gas Product, g/kg Arabinose								
Gas Product Yield, wt. %	24.0	22.3	20.8	19.7	40.0	38.5	37.8	36.0
Aqueous Product Yield, wt. %	26.9	27.3	27.6	28.0	26.8	27.3	27.9	28.2
Solid Product Yield (Coke+Tar), wt. %	47.5	49.6	50.0	50.7	30.2	31.6	33.9	35.3
TOC of Aqueous Product, mg/L	1280	1295	1310	1330	1275	1300	1325	1345
Amount of Coke, g/kg Arabinose	283.4	291.8	300.1	304.3	170.9	179.2	191.7	200.1

Table 24. Experimental results of Arabinose SCWG at 500°C for the pressures 200, 275, 350, 425 atm without and with K₂CO₃.

Experiment No	133	134	135	136	137	138	139	140
Reaction Temperature, °C	500	500	500	500	500	500	500	500
Reaction Pressure, atm	210	280	355	435	200	285	360	440
Arabinose/Water	0.65/8.1	0.9/11.25	1.2/15.0	1.6/20.0	0.65/8.1	0.9/11.25	1.2/15.0	1.6/20.0
Catalyst, 10 wt. %	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Gas Composition, % mol								
CH ₄	15.6	17.5	19.2	22.0	13.7	17.2	19.7	22.1
H ₂	27.5	26.1	25.7	24.1	37.5	31.3	28.8	25.2
CO ₂	50.2	49.8	48.5	46.4	44.1	46.1	44.6	45.2
CO	2.1	1.4	0.8	0.5	1.2	0.8	0.5	0.3
C ₂ -C ₄	4.6	5.2	5.8	7.0	3.5	4.6	6.4	7.2
Gas Product, mol/ kg Arabinose								
CH ₄	3.2	3.4	3.6	3.8	4.3	4.4	4.8	5.0
H ₂	5.7	5.1	4.8	4.2	11.8	8.4	7.1	5.9
CO ₂	10,4	9,6	9,0	8,1	13,8	11,9	11,0	10,5
CO	0.4	0.26	0.14	0.08	0.3	0.2	0.1	0.07
C ₂ -C ₄	0.9	1.0	1.1	1.2	0.9	1.2	1.3	1.6
Gas Product, g/kg Arabinose								
Gas Product Yield, wt. %	49.9	47.9	46.8	45.0	64.5	62.3	60.8	59.5
Aqueous Product Yield, wt. %	20.6	22.3	22.7	23.1	13.4	14.0	14.5	14.8
Solid Product Yield (Coke+Tar), wt. %	25.0	27.2	29.1	30.2	17.9	19.2	20.6	21.3
TOC of Aqueous Product, mg/L	980	1060	1080	1095	640	665	690	705
Amount of Coke, g/kg Arabinose	141.7	154.2	165.0	170.9	101.7	108.3	116.7	120.0

Table 25. Experimental results of Arabinose SCWG at 600°C for the pressures 200, 275, 350, 425 atm without and with K₂CO₃.

Experiment No	141	142	143	144	145	146	147	148
Reaction Temperature, °C	600	600	600	600	600	600	600	600
Reaction Pressure, atm	195	280	345	420	190	280	340	430
Arabinose/Water	0.55/6.9	0.8/10.0	0.9/11.25	1.1/13.75	0.55/6.9	0.8/10.0	0.9/11.25	1.1/13.75
Catalyst, 10 wt. %	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Gas Composition, % mol								
CH ₄	19.4	22.7	24.8	27.8	14.0	15.4	18.1	20.9
H ₂	31.8	31.2	30.7	28.2	43.9	41.5	41.1	37.5
CO ₂	45.5	42.7	40.8	38.8	39.9	40.2	37.5	37.7
CO	1.0	0.8	0.6	0.4	1.0	0.8	0.6	0.3
C ₂ -C ₄	2.3	2.6	3.1	4.8	1.2	2.1	2.7	3.5
Gas Product, mol/ kg Arabinose								
CH ₄	6.3	7.2	7.6	7.8	7.5	7.7	8.2	8.6
H ₂	10.3	9.9	9.4	7.9	23.6	20.7	18.6	15.4
CO ₂	14,9	13,5	12,5	10,9	21,5	20,0	17,0	15,5
CO	0.3	0.25	0.17	0.11	0.5	0.4	0.27	0.1
C ₂ -C ₄	0.7	0.8	0.9	1.4	0.6	1.0	1.2	1.4
Gas Product, g/kg Arabinose								
Gas Product Yield, wt. %	813.4	768.0	731.2	677.2	1151.2	1075.8	955.4	909.2
Aqueous Product Yield, wt. %	70.8	69.7	68.5	67.3	94.5	93.1	86.5	84.4
Solid Product Yield (Coke+Tar), wt. %	6.0	6.4	6.8	7.4	3.8	4.3	4.6	5.3
TOC of Aqueous Product, mg/L	22.1	23.1	23.8	25.0	1.4	2.2	4.6	6.1
TOC of Aqueous Product, mg/L	285	305	325	350	180	205	220	250
Amount of Coke, g/kg Arabinose	125.1	130.9	135.1	141.7	8.3	12.5	25.8	35.0

Table 26. Experimental results of Tannic acid SCWG at 400°C for the pressures 200, 275, 350, 425 atm without and with K₂CO₃.

Experiment No	149	150	151	152	153	154	155	156
Reaction Temperature, °C	400	400	400	400	400	400	400	400
Reaction Pressure, atm	201	277	353	428	200	280	356	432
Xylose/Water	0.9/11.25	1.6/20	2.6/32.5	3.5/43.75	0.9/11.25	1.6/20	2.6/32.5	3.5/43.75
Catalyst, 10 wt. %	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Gas Composition, % mol								
CH ₄	1.3	2.1	3.4	4.6	5.1	5.6	7.4	8.8
H ₂	14.6	12.5	10.1	8.8	22.7	21.6	19.3	15.9
CO ₂	74.5	80.2	82.2	83.0	69.9	70.1	70.2	71.4
CO	8.0	3.0	1.5	0.2	0.5	0.4	0.3	0.2
C ₂ -C ₄	1.6	2.2	2.8	3.4	1.8	2.3	2.8	3.7
Gas Product, mol/ kg Tannic acid								
CH ₄	0.2	0.3	0.4	0.5	1.4	1.5	1.7	1.8
H ₂	2.4	1.8	1.2	0.9	6.3	5.6	4.6	3.3
CO ₂	12.4	11.7	10.1	8.8	19.5	18.2	16.6	14.7
CO	1.3	0.4	0.2	0.02	0.13	0.1	0.07	0.04
C ₂ -C ₄	0.23	0.32	0.34	0.36	0.5	0.6	0.7	0.8
Gas Product, g/kg Tannic acid								
Gas Product Yield, wt. %	32.8	29.7	26.1	23.0	50.1	47.8	44.5	41.3
Aqueous Product Yield, wt. %	32.9	33.8	35.5	36.4	20.5	21.6	23.0	24.5
Solid Product Yield (Coke+Tar), wt. %	29.8	33.0	35.0	37.4	27.1	28.9	30.2	32.3
TOC of Aqueous Product, mg/L	1740.0	1805.0	1895.0	1945.0	1096.0	1154.0	1225.0	1310.0
Amount of Coke, g/kg Tannic acid	177.7	207.1	219.8	235.0	181.1	192.5	201.6	215.5

Table 27. Experimental results of Tannic acid SCWG at 500°C for the pressures 200, 275, 350, 425 atm without and with K₂CO₃.

Experiment No	157	158	159	160	161	162	163	164
Reaction Temperature, °C	500	500	500	500	500	500	500	500
Reaction Pressure, atm	208	281	349	424	204	277	353	428
Xylose/Water	0.65/8.1	0.9/11.25	1.2/15	1.6/20	0.65/8.1	0.9/11.25	1.2/15	1.6/20
Catalyst, 10 wt. %	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Gas Composition, % mol								
CH ₄	8.3	10.5	12.7	14.4	10.6	12.0	13.9	16.1
H ₂	28.1	23.1	20.1	19.1	35.6	33.9	28.6	24.3
CO ₂	60.7	61.6	61.4	59.4	50.2	50.0	53.0	54.3
CO	0.5	0.4	0.3	0.2	0.8	0.6	0.3	0.1
C ₂ -C ₄	2.4	4.4	5.5	6.9	2.8	3.5	4.2	5.2
Gas Product, mol/ kg Tannic acid								
CH ₄	2.6	2.8	3.1	3.3	4.7	4.9	5.1	5.4
H ₂	8.9	6.3	4.9	4.3	15.8	13.9	10.5	8.1
CO ₂	19.3	16.7	14.8	13.6	22.3	20.6	19.5	18.1
CO	0.15	0.1	0.07	0.05	0.32	0.22	0.10	0.03
C ₂ -C ₄	0.8	1.2	1.3	1.6	1.1	1.4	1.5	1.7
Gas Product, g/kg Tannic acid								
Gas Product Yield, wt. %	53.8	50.7	47.7	46.1	68.4	66.2	64.2	62.5
Aqueous Product Yield, wt. %	17.1	18.9	20.3	21.6	11.7	12.5	13.6	14.3
Solid Product Yield (Coke+Tar), wt. %	25.2	27.2	29.6	30.7	15.5	18.1	20.9	21.8
TOC of Aqueous Product, mg/L	915.0	1010.0	1085.0	1155.0	625.0	670.0	725.0	765.0
Amount of Coke, g/kg Tannic acid	153.2	164.9	179.6	205.6	110.5	128.5	139.6	154.8

Table 28. Experimental results of Tannic acid SCWG at 600°C for the pressures 200, 275, 350, 425 atm without and with K₂CO₃.

Experiment No	165	166	167	168	169	170	171	172
Reaction Temperature, °C	600	600	600	600	600	600	600	600
Reaction Pressure, atm	206	277	348	426	205	276	353	431
Xylose/Water	0.55/6.9	0.8/10.0	0.9/11.25	1.1/13.75	0.55/6.9	0.8/10.0	0.9/11.25	1.1/13.75
Catalyst, 10 wt. %	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Gas Composition, % mol								
CH ₄	13.7	16.8	19.1	21.5	15.7	17.8	19.5	20.8
H ₂	38.7	32.5	28.4	24.9	40.1	39.8	37.5	37.0
CO ₂	45.5	47.8	48.6	48.9	41.6	39.4	39.5	38.0
CO	0.6	0.5	0.4	0.3	0.7	0.5	0.3	0.2
C ₂ -C ₄	1.5	2.4	3.5	4.4	1.9	2.5	3.2	4.4
Gas Product, mol/ kg Tannic acid								
CH ₄	7.0	7.4	7.6	7.8	9.7	10.2	10.5	10.8
H ₂	19.8	14.3	11.3	9.0	24.7	22.7	20.2	19.3
CO ₂	23.2	21.1	19.3	17.8	25.6	22.5	21.3	19.8
CO	0.3	0.2	0.16	0.1	0.7	0.5	0.3	0.2
C ₂ -C ₄	0.8	1.0	1.4	1.6	1.1	1.4	1.7	2.0
Gas Product, g/kg Tannic acid								
Gas Product Yield, wt. %	73.2	70.4	68.6	66.6	87.9	83.9	82.3	81.6
Aqueous Product Yield, wt. %	8.9	9.7	10.4	11.6	5.5	6.3	6.9	7.4
Solid Product Yield (Coke+Tar), wt. %	14.5	16.2	17.7	20.6	5.6	7.1	8.4	10.1
TOC of Aqueous Product, mg/L	480.0	519.0	558.0	621.0	295.0	335.0	370.0	395.0
Amount of Coke, g/kg Tannic acid	103.1	115.0	126.2	138.1	39.5	51.1	60.1	71.9

Table 29. Experimental results of Gallic acid SCWG at 400°C for the pressures 200, 275, 350, 425 atm without and with K₂CO₃.

Experiment No	173	174	175	176	177	178	179	180
Reaction Temperature, °C	400	400	400	400	400	400	400	400
Reaction Pressure, atm	210	280	355	440	205	280	360	430
Catalyst, 10 wt. %	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Gas Composition, % mol								
CH ₄	1.7	2.4	2.8	4.0	2.6	3.8	5.7	7.9
H ₂	14.6	13.8	12.5	10.7	23.4	18.1	16.2	14.4
CO ₂	80.7	80.3	80.6	80.3	71.5	74.8	74.0	73.0
CO	0.9	0.7	0.5	0.4	0.6	0.4	0.2	0.1
C ₂ -C ₄	2.1	2.8	3.4	4.6	1.9	2.9	3.9	4.2
Gas Product, mol/ kg P Gallic acid								
CH ₄	0.3	0.35	0.4	0.5	0.7	0.9	1.2	1.5
H ₂	2.2	2.0	1.7	1.3	6.5	4.4	3.5	2.8
CO ₂	12.4	11.7	11.3	10.0	20.0	18.2	15.8	14.0
CO	0.1	0.09	0.07	0.05	0.2	0.1	0.04	0.02
C ₂ -C ₄	0.3	0.4	0.5	0.6	0.5	0.7	0.8	0.9
Gas Product, g/kg Gallic acid								
Gas Product Yield, wt. %	33.3	31.9	30.6	28.9	53.9	51.2	46.4	43.1
Aqueous Product Yield, wt. %	34.9	35.4	36.0	36.6	20.2	21.7	23.3	24.3
Solid Product Yield (Coke+Tar), wt. %	27.9	29.0	30.1	31.6	22.2	22.5	26.4	29.0
TOC of Aqueous Product, mg/L	1850.0	1880.0	1910.0	1940.0	1070.0	1150.0	1235.0	1305.0
Amount of Coke, g/kg Gallic acid	165.7	175.0	186.2	195.5	130.4	137.8	153.6	175.1

Table 30. Experimental results of Gallic acid SCWG at 500°C for the pressures 200, 275, 350, 425 atm without and with K₂CO₃.

Experiment No	181	182	183	184	185	186	187	188
Reaction Temperature, °C	500	500	500	500	500	500	500	500
Reaction Pressure, atm	215	275	360	425	210	280	350	435
Catalyst, 10 wt. %	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Gas Composition, % mol								
CH₄	8.2	9.7	10.9	13.2	8.9	10.9	12.4	14.9
H₂	29.2	24.1	22.7	19.2	34.7	33.3	30.6	25.0
CO₂	59.3	61.4	61.0	61.1	52.4	51.1	51.5	53.6
CO	0.6	0.4	0.2	0.1	0.8	0.6	0.3	0.2
C₂-C₄	2.7	4.4	5.2	6.4	3.2	4.1	5.2	0.06
Gas Product, mol/ kg Gallic acid								
CH₄	2.0	2.1	2.3	2.5	3.4	3.9	4.1	4.4
H₂	7.3	5.3	4.8	3.7	13.5	12.1	10.2	7.4
CO₂	14.8	13.6	13.0	11.7	20.4	18.4	17.0	15.8
CO	0.14	0.09	0.04	0.02	0.3	0.2	0.1	0.06
C₂-C₄	0.7	1.0	1.1	1.2	1.3	1.5	1.7	1.9
Gas Product, g/kg Gallic acid								
Gas Product Yield, wt. %	46.1	44.9	40.0	42.1	65.2	63.9	62.1	59.5
Aqueous Product Yield, wt. %	29.4	29.6	30.3	31.1	16.4	17.6	18.8	19.2
Solid Product Yield (Coke+Tar), wt. %	20.3	21.9	22.6	23.3	14.5	15.2	16.6	18.1
TOC of Aqueous Product, mg/L	1560.0	1590.0	1610.0	1650.0	870.0	935.0	998.0	1020.0
Amount of Coke, g/kg Gallic acid	125.6	135.0	139.6	144.3	93.1	97.7	97.7	1164.4

Table 31. Experimental results of Gallic acid SCWG at 600°C for the pressures 200, 275, 350, 425 atm without and with K₂CO₃.

Experiment No	189	190	191	192	193	194	195	196
Reaction Temperature, °C	600	600	600	600	600	600	600	600
Reaction Pressure, atm	210	285	360	430	205	280	355	440
Catalyst, 10 wt. %	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Gas Composition, % mol								
CH ₄	13.1	16.8	18.8	20.8	13.3	16.7	18.5	20.8
H ₂	40.0	34.1	29.9	25.3	44.4	41.4	37.7	36.5
CO ₂	44.3	45.5	46.9	48.6	39.9	38.7	39.4	37.6
CO	0.5	0.4	0.3	0.1	0.6	0.3	0.2	0.2
C ₂ -C ₄	2.1	3.2	4.1	5.2	1.8	2.9	4.2	4.9
Gas Product, mol/ kg Gallic acid								
CH ₄	6.6	7.2	7.4	7.2	8.2	9.2	9.3	9.8
H ₂	20.0	14.7	11.8	8.8	27.4	22.7	18.9	17.4
CO ₂	21.5	19.6	18.6	16.9	24.5	21.4	19.7	17.9
CO	0.2	0.16	0.11	0.04	0.4	0.2	0.1	0.1
C ₂ -C ₄	1.1	1.4	1.6	1.8	1.1	1.5	2.1	2.4
Gas Product, g/kg Gallic acid								
Gas Product Yield, wt. %	77.1	74.1	73.3	69.4	87.2	84.7	83.3	82.1
Aqueous Product Yield, wt. %	10.2	11.2	12.2	13.6	4.5	5.0	5.3	5.7
Solid Product Yield (Coke+Tar), wt. %	8.5	9.9	12.0	14.7	6.6	7.9	9.2	10.5
TOC of Aqueous Product, mg/L	540.0	595.0	650	720.0	240.0	265.0	280.0	305.0
Amount of Coke, g/kg Gallic acid	55.8	65.1	79.1	93.1	46.5	55.8	65.2	74.4

Table 32. Experimental results of Phloroglucinol SCWG at 400°C for the pressures 200, 275, 350, 425 atm without and with K₂CO₃.

Experiment No	197	198	199	200	201	202	203	204
Reaction Temperature, °C	400	400	400	400	400	400	400	400
Reaction Pressure, atm	200	270	355	420	200	270	345	420
Catalyst, 10 wt. %	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Gas Composition, % mol								
CH ₄	2.7	4.2	5.2	7.7	8.6	10.6	15.4	18.9
H ₂	4.2	2.8	1.6	1.0	7.8	3.2	1.6	0.9
CO ₂	90.7	90.5	90.8	88.6	81.2	83.5	80.7	77.4
CO	1.9	1.5	0.8	0.6	1.8	1.5	0.6	0.2
C ₂ -C ₄	0.5	1.0	1.6	2.1	0.6	1.2	1.7	2.2
Gas Product, mol/ kg Phloroglucinol								
CH ₄	0.5	0.7	0.8	1.1	2.0	2.3	3.1	3.4
H ₂	1.8	0.5	0.2	0.1	1.9	0.7	0.3	0.2
CO ₂	17.3	14.8	13.6	12.1	19.4	18.0	16.2	13.8
CO	0.4	0.3	0.1	0.08	0.4	0.3	0.1	0.03
C ₂ -C ₄	0.1	0.2	0.25	0.3	0.1	0.2	0.3	0.4
Gas Product, g/kg Phloroglucinol								
Gas Product, g/kg Phloroglucinol	788.0	679.8	624.4	564.4	904.6	846.6	777.8	678.8
Gas Product Yield, wt. %	38.8	34.1	31.8	29.3	46.7	44.8	42.5	38.1
Aqueous Product Yield, wt. %	43.6	47.1	48.0	49.3	40.2	41.1	41.9	43.1
Solid Product Yield (Coke+Tar), wt. %	13.5	15.6	20.2	21.8	9.5	11.1	12.7	16.8
TOC of Aqueous Product, mg/L	2280.0	2465.0	2510.0	2580.0	2105.0	2150.0	2190.0	2250.0
Amount of Coke, g/kg Phloroglucinol	87.4	109.3	131.1	142.1	65.6	76.5	87.4	109.3

Table 33. Experimental results of Phloroglucinol SCWG at 500°C for the pressures 200, 275, 350, 425 atm without and with K₂CO₃.

Experiment No	205	206	207	208	209	210	211	212
Reaction Temperature, °C	500	500	500	500	500	500	500	500
Reaction Pressure, atm	195	270	350	420	202	275	355	430
Catalyst, 10 wt. %	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Gas Composition, % mol								
CH ₄	24.2	26.9	29.1	32.9	21.0	23.7	30.3	37.6
H ₂	13.9	11.3	9.3	8.8	29.7	22.7	19.2	12.1
CO ₂	55.5	58.6	59.2	55.8	47.6	52.0	46.7	47.8
CO	5.8	2.4	1.2	0.8	1.1	0.8	0.6	0.3
C ₂ -C ₄	0.6	0.8	1.2	1.7	0.6	0.8	1.6	2.2
Gas Product, mol/ kg Phloroglucinol								
CH ₄	8.4	8.5	8.6	9.1	9.0	9.1	11.3	11.8
H ₂	4.8	3.6	2.8	2.4	11.8	8.7	6.8	3.8
CO ₂	19.2	18.5	17.5	15.5	20.4	19.9	16.5	15.0
CO	2.0	0.8	0.4	0.2	0.4	0.3	0.2	0.09
C ₂ -C ₄	0.2	0.3	0.4	0.5	0.2	0.3	0.6	0.7
Gas Product, g/kg Phloroglucinol								
Gas Product, g/kg Phloroglucinol	1052.8	991.6	940.4	858.0	1084.4	1059.2	950.2	886.9
Gas Product Yield, wt. %	63.2	59.8	57.6	54.7	64.6	63.0	61.7	60.2
Aqueous Product Yield, wt. %	23.8	25.2	28.3	31.4	24.8	25.2	26.4	29.8
Solid Product Yield (Coke+Tar), wt. %	8.9	10.5	11.5	13.0	6.6	6.7	7.9	9.5
TOC of Aqueous Product, mg/L	1245.0	1320.0	1480.0	1645.0	1295.0	1320.0	1380.0	1558.0
Amount of Coke, g/kg Phloroglucinol	60.1	71.0	81.9	92.9	43.7	49.1	54.6	65.5

Table 34. Experimental results of Phloroglucinol SCWG at 600°C for the pressures 200, 275, 350, 425 atm without and with K₂CO₃.

Experiment No	213	214	215	216	217	218	219	220
Reaction Temperature, °C	600	600	600	600	600	600	600	600
Reaction Pressure, atm	205	280	350	420	201	280	350	415
Catalyst, 10 wt. %	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Gas Composition, % mol								
CH ₄	32.1	39.1	41.1	42.9	14.1	23.8	28.4	32.8
H ₂	20.7	14.8	13.7	12.1	47.6	35.1	28.0	22.6
CO ₂	45.3	44.6	43.8	43.1	36.2	38.7	41.0	38.6
CO	1.3	0.6	0.2	0.1	1.4	1.0	0.6	0.2
C ₂ -C ₄	0.6	0.9	1.2	1.8	0.7	1.4	2.0	2.2
Gas Product, mol/ kg Phloroglucinol								
CH ₄	16.1	17.8	18.2	18.4	11.8	15.8	16.4	19.4
H ₂	10.3	6.7	6.1	5.3	39.8	23.2	16.2	11.9
CO ₂	22.7	20.3	19.3	18.2	30.2	25.6	23.7	20.4
CO	0.6	0.3	0.1	0.03	1.2	0.7	0.3	0.1
C ₂ -C ₄	0.3	0.4	0.5	0.8	0.6	0.9	1.2	1.3
Gas Product, g/kg Phloroglucinol								
Gas Product, g/kg Phloroglucinol	1305.8	1215.4	1175.4	1138.6	1654.8	1481.2	1394.0	1286.6
Gas Product Yield, wt. %	84.5	82.8	81.8	80.5	94.7	93.3	91.1	89.9
Aqueous Product Yield, wt. %	6.3	6.6	7.0	8.1	3.7	2.2	2.9	5.7
Solid Product Yield (Coke+Tar), wt. %	4.8	6.5	8.1	8.8	1.5	1.9	2.4	2.9
TOC of Aqueous Product, mg/L	330.0	345.0	365.0	390.0	180.0	120.0	155.0	300.0
Amount of Coke, g/kg Phloroglucinol	32.8	43.7	54.6	65.6	12.5	15.1	17.2	19.6

Table 35. Experimental results of Pyrogallol SCWG at 400°C for the pressures 200, 275, 350, 425 atm without and with K₂CO₃.

Experiment No	221	222	223	224	225	226	227	228
Reaction Temperature, °C	400	400	400	400	400	400	400	400
Reaction Pressure, atm	195	270	345	420	205	270	345	425
Catalyst, 10 wt. %	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Gas Composition, % mol								
CH ₄	1.1	2.2	4.9	6.8	3.6	4.9	6.2	7.1
H ₂	18.5	14.9	13.2	12.1	17.8	17.1	16.8	11.9
CO ₂	68.8	78.2	76.2	74.7	74.1	73.0	71.3	74.7
CO	9.5	1.8	1.1	0.7	1.2	0.8	0.4	0.2
C ₂ -C ₄	2.1	2.9	4.6	5.7	3.3	4.2	5.3	6.1
Gas Product, mol/ kg Pyrogallol								
CH ₄	0.2	0.3	0.5	0.6	0.7	0.9	1.0	1.1
H ₂	2.8	1.9	1.4	1.0	3.7	3.2	2.7	1.7
CO ₂	10.4	9.8	7.8	6.5	15.5	13.7	11.3	11.2
CO	1.4	0.2	0.1	0.01	0.3	0.2	0.1	0.03
C ₂ -C ₄	0.3	0.4	0.5	0.55	0.6	0.7	0.8	0.9
Gas Product, g/kg Pyrogallol	517.6	461.4	376.8	319.9	732.8	659.9	553.4	550.6
Gas Product Yield, wt. %	26.7	23.6	20.1	17.4	38.2	35.1	31.2	30.7
Aqueous Product Yield, wt. %	42.4	43.5	44.6	45.6	34.9	35.8	36.4	37.1
Solid Product Yield (Coke+Tar), wt. %	29.7	30.9	32.0	33.6	25.0	25.9	28.1	28.9
TOC of Aqueous Product, mg/L	2850.0	2925.0	2998.0	3065.0	2345.0	2405.0	2445.0	2490.0
Amount of Coke, g/kg Pyrogallol	212.5	221.1	228.7	239.8	178.5	187.0	195.5	206.6

Table 36. Experimental results of Pyrogallol SCWG at 500°C for the pressures 200, 275, 350, 425 atm without and with K₂CO₃.

Experiment No	229	230	231	232	233	234	235	236
Reaction Temperature, °C	500	500	500	500	500	500	500	500
Reaction Pressure, atm	200	280	355	430	200	275	345	430
Catalyst, 10 wt. %	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Gas Composition, % mol								
CH ₄	9.4	10.9	11.5	15.2	12.2	15.2	17.3	20.0
H ₂	30.6	28.4	23.9	21.3	47.2	37.8	33.8	27.0
CO ₂	54.3	51.9	54.5	52.5	37.4	42.4	43.5	46.2
CO	0.7	0.6	0.5	0.3	1.0	0.8	0.6	0.4
C ₂ -C ₄	5.0	8.2	9.6	10.7	2.2	3.8	4.8	6.4
Gas Product, mol/ kg Pyrogallol								
CH ₄	2.2	2.4	2.5	2.6	5.6	5.7	5.8	6.0
H ₂	7.5	6.1	4.5	3.7	21.5	14.0	11.5	8.2
CO ₂	13.2	11.2	10.2	9.1	17.0	15.9	14.9	13.9
CO	0.17	0.12	0.09	0.05	0.5	0.3	0.2	0.1
C ₂ -C ₄	1.2	1.7	1.8	1.9	1.1	1.4	1.7	1.9
Gas Product, g/kg Pyrogallol								
Gas Product Yield, wt. %	39.4	37.9	36.9	34.5	55.2	54.0	52.8	51.8
Aqueous Product Yield, wt. %	31.8	32.4	32.8	33.6	25.4	26.0	27.2	28.1
Solid Product Yield (Coke+Tar), wt. %	24.3	25.6	28.3	29.8	15.1	15.6	16.7	18.4
TOC of Aqueous Product, mg/L	2135.0	2180.0	2205.0	2255.0	1705.0	1745.0	1825.0	1885.0
Amount of Coke, g/kg Pyrogallol	165.8	178.6	202.3	212.5	114.7	119.0	127.5	136.0

Table 37. Experimental results of Pyrogallol SCWG at 600°C for the pressures 200, 275, 350, 425 atm without and with K₂CO₃.

Experiment No	237	238	239	240	241	242	243	244
Reaction Temperature, °C	600	600	600	600	600	600	600	600
Reaction Pressure, atm	200	280	350	420	201	280	345	430
Catalyst, 10 wt. %	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Gas Composition, % mol								
CH ₄	9.7	13.2	15.0	17.2	16.3	18.0	19.1	20.7
H ₂	36.4	29.1	25.4	23.8	48.4	46.7	43.8	41.9
CO ₂	48.1	52.8	53.6	51.9	34.1	33.9	35.4	35.3
CO	0.9	0.6	0.4	0.2	0.5	0.4	0.3	0.1
C ₂ -C ₄	2.9	4.3	5.6	6.9	0.5	1.0	1.4	2.0
Gas Product, mol/ kg Pyrogallol								
CH ₄	4.2	5.1	5.3	5.6	12.2	12.4	12.6	12.7
H ₂	13.5	11.2	8.9	7.9	36.1	33.0	29.6	26.0
CO ₂	20.6	20.4	18.9	17.1	25.5	23.9	23.4	21.9
CO	0.4	0.3	0.2	0.06	0.3	0.2	0.2	0.07
C ₂ -C ₄	1.2	1.7	2.0	2.2	0.5	0.8	1.0	1.2
1								
Gas Product, g/kg Pyrogallol	1059.8	1078.0	1019.8	947.5	1418.0	1353.6	1336.1	1268.8
Gas Product Yield, wt. %	64.2	63.1	61.3	60.0	83.0	81.4	80.9	79.8
Aqueous Product Yield, wt. %	14.5	15.0	16.2	16.5	4.0	4.2	4.4	4.8
Solid Product Yield (Coke+Tar), wt. %	17.7	17.9	19.1	20.2	8.3	9.5	10.7	11.9
TOC of Aqueous Product, mg/L	975.0	1010.0	1090.0	1110.0	269.0	280.0	295.0	320.0
Amount of Coke, g/kg Pyrogallol	123.0	127.5	136.1	144.5	59.5	68.0	76.5	85.0

Table 38. Experimental results of Pectin SCWG at 400°C for the pressures 200, 275, 350, 425 atm without and with K₂CO₃.

Experiment No	245	246	247	248	249	250	251	252
Reaction Temperature, °C	400	400	400	400	400	400	400	400
Reaction Pressure, atm	201	278	352	424	200	270	345	420
Catalyst, 10 wt. %	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Gas Composition, % mol								
CH ₄	2.5	3.2	4.1	5.3	2.8	3.7	4.9	5.8
H ₂	28.4	26.5	21.8	18.4	30.6	27.2	23.8	21.8
CO ₂	67.0	68.0	71.3	72.7	64.4	66.8	68.5	68.6
CO	1.1	0.8	0.5	0.2	0.9	0.7	0.4	0.2
C ₂ -C ₄	1.0	1.5	2.3	3.4	1.3	1.6	2.4	3.6
Gas Product, mol/ kg Pectin								
CH ₄	0.3	0.4	0.5	0.6	0.4	0.5	0.6	0.7
H ₂	3.8	3.1	2.3	1.5	5.5	4.3	3.3	2.7
CO ₂	9.1	8.0	7.2	6.5	11.6	10.6	9.4	8.7
CO	0.14	0.08	0.05	0.02	0.15	0.1	0.05	0.02
C ₂ -C ₄	0.1	0.18	0.24	0.4	0.15	0.25	0.4	0.5
Gas Product, g/kg Pectin								
Gas Product Yield, wt. %	31.8	28.9	26.8	25.2	41.0	38.4	36.1	34.7
Aqueous Product Yield, wt. %	28.3	29.3	30.3	31.6	33.8	35.0	36.2	37.1
Solid Product Yield (Coke+Tar), wt. %	36.4	40.5	42.5	42.5	23.2	24.7	26.3	27.5
TOC of Aqueous Product, mg/L	1050	1085	1120	1170	1250	1295	1340	1372
Amount of Coke, g/kg Pectin	180.1	201.1	214.2	225.4	110.2	122.3	130.2	137.6

Table 39. Experimental results of Pectin SCWG at 500°C for the pressures 200, 275, 350, 425 atm without and with K₂CO₃.

Experiment No	253	254	255	256	257	258	259	260
Reaction Temperature, °C	500	500	500	500	500	500	500	500
Reaction Pressure, atm	209	281	354	428	208	279	353	426
Catalyst, 10 wt. %	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Gas Composition, % mol								
CH ₄	9.3	11.1	12.9	16.3	8.8	10.2	12.7	14.1
H ₂	11.4	39.2	34.1	33.4	45.1	42.7	38.3	35.1
CO ₂	45.0	46.4	49.2	45.7	43.2	43.8	45.4	46.2
CO	0.9	0.7	0.5	0.2	0.6	0.6	0.4	0.2
C ₂ -C ₄	1.7	2.6	3.3	4.4	2.3	2.8	3.2	4.4
Gas Product, mol/ kg Pectin								
CH ₄	2.5	2.6	3.0	3.1	3.0	3.2	3.5	3.6
H ₂	11.4	9.3	8.1	6.4	15.6	13.3	10.8	8.9
CO ₂	12.0	11.1	10.7	8.8	15.0	13.7	12.8	11.7
CO	0.23	0.16	0.1	0.04	0.2	0.14	0.1	0.05
C ₂ -C ₄	0.5	0.6	0.8	0.9	0.7	0.8	0.9	1.1
Gas Product, g/kg Pectin								
Gas Product Yield, wt. %	52.5	49.8	47.8	45.5	65.7	62.6	60.6	58.8
Aqueous Product Yield, wt. %	16.2	17.0	17.8	19.1	13.4	14.3	15.5	16.4
Solid Product Yield (Coke+Tar), wt. %	27.3	29.3	32.4	34.2	17.2	19.5	21.6	23.3
TOC of Aqueous Product, mg/L	600	630	660	705	495	528	575	610
Amount of Coke, g/kg Pectin	129.9	145.3	160.0	169.2	85.0	96.1	108.3	120.4

Table 40. Experimental results of Pectin SCWG at 600°C for the pressures 200, 275, 350, 425 atm without and with K₂CO₃.

Experiment No	261	262	263	264	265	266	267	268
Reaction Temperature, °C	600	600	600	600	600	600	600	600
Reaction Pressure, atm	201	281	353	424	195	281	354	425
Catalyst, 10 wt. %	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Gas Composition, % mol								
CH ₄	7.6	8.9	10.7	13.5	14.2	15.7	17.5	21.5
H ₂	44.5	41.4	39.6	34.2	48.4	46.8	44.6	40.4
CO ₂	45.9	47.4	47.2	49.6	36.2	35.8	35.8	35.3
CO	0.6	0.5	0.4	0.2	0.5	0.4	0.3	0.2
C ₂ -C ₄	1.4	1.8	2.1	2.6	0.7	1.3	1.8	2.6
Gas Product, mol/ kg Pectin								
CH ₄	2.8	3.0	3.4	3.8	7.3	7.5	7.8	8.4
H ₂	16.1	13.8	12.6	9.8	25.2	22.5	19.8	15.7
CO ₂	16.7	15.8	15.0	14.1	18.8	17.3	15.9	13.7
CO	0.2	0.16	0.12	0.06	0.26	0.2	0.13	0.08
C ₂ -C ₄	0.5	0.6	0.7	0.8	0.3	0.6	0.8	1.0
Gas Product, g/kg Pectin								
Gas Product, g/kg Pectin	837.4	799.3	771.0	734.9	1013.7	955.8	899.6	810.8
Gas Product Yield, wt. %	69.9	66.4	65.5	64.2	88.6	86.2	83.6	80.5
Aqueous Product Yield, wt. %	4.3	5.4	7.1	8.2	2.6	3.2	4.3	4.8
Solid Product Yield (Coke+Tar), wt. %	21.6	22.3	25.3	26.3	5.6	7.2	8.8	10.5
TOC of Aqueous Product, mg/L	160	200	260	305	95	120	160	180
Amount of Coke, g/kg Pectin	100	115.1	126.3	138.2	30.7	38.2	45.3	54.1

Table 41. Experimental results of Galacturonic acid SCWG at 400°C for the pressures 200, 275, 350, 425 atm without and with K₂CO₃.

Experiment No	269	270	271	272	273	274	275	276
Reaction Temperature, °C	400	400	400	400	400	400	400	400
Reaction Pressure, atm	201	278	352	424	200	270	345	420
Catalyst, 10 wt. %	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Gas Composition, % mol								
CH ₄	3.8	4.5	5.8	7.2	6.0	6.9	7.8	8.6
H ₂	21.7	17.6	13.1	11.7	24.9	19.8	18.1	15.8
CO ₂	71.8	75.1	78.1	77.8	66.0	70.0	70.9	73.2
CO	1.2	0.9	0.6	0.4	1.6	1.2	0.8	0.4
C ₂ -C ₄	1.5	1.9	2.4	2.9	1.5	2.1	2.4	2.8
Gas Product, mol/ kg Pectin								
CH ₄	0.5	0.6	0.7	0.8	1.0	1.1	1.2	1.3
H ₂	3.0	2.2	1.5	1.2	4.2	3.9	2.8	2.3
CO ₂	9.9	9.7	9.8	8.1	11.2	11.0	10.9	10.7
CO	0.2	0.1	0.07	0.04	0.27	0.19	0.12	0.06
C ₂ -C ₄	0.2	0.24	0.28	0.3	0.25	0.33	0.37	0.41
Gas Product, g/kg Pectin								
Gas Product Yield, wt. %	36.2	35.2	33.9	31.1	42.5	41.5	40.8	40.2
Aqueous Product Yield, wt. %	18.6	19.5	20.1	22.5	17.8	18.6	18.9	19.1
Solid Product Yield (Coke+Tar), wt. %	41.3	42.3	43.3	45.4	37.1	39.2	39.9	40.9
TOC of Aqueous Product, mg/L	720	755	780	825	690	720	730	740
Amount of Coke, g/kg Pectin	191.5	196.3	201.2	210.7	172.4	182.0	184.8	189.6

Table 42. Experimental results of Galacturonic acid SCWG at 500°C for the pressures 200, 275, 350, 425 atm without and with K₂CO₃.

Experiment No	277	278	279	280	281	282	283	284
Reaction Temperature, °C	500	500	500	500	500	500	500	500
Reaction Pressure, atm	209	281	354	428	208	279	353	426
Catalyst, 10 wt. %	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Gas Composition, % mol								
CH ₄	8.7	10.1	11.5	13.5	8.8	11.5	14.7	16.8
H ₂	29.5	26.0	21.8	18.1	35.3	31.5	28.4	23.6
CO ₂	59.5	60.8	63.4	64.5	53.0	53.6	52.6	54.4
CO	0.7	0.5	0.2	0.2	0.8	0.5	0.4	0.4
C ₂ -C ₄	1.6	2.6	3.1	3.7	2.1	2.9	3.9	4.8
Gas Product, mol/ kg Pectin								
CH ₄	1.7	1.8	1.9	2.1	2.6	3.1	3.6	3.8
H ₂	5.8	4.7	3.6	2.8	10.4	8.4	7.0	5.4
CO ₂	11.8	10.8	10.3	9.7	15.6	14.4	13.0	12.4
CO	0.1	0.07	0.05	0.02	0.22	0.13	0.1	0.09
C ₂ -C ₄	0.3	0.4	0.5	0.6	0.7	0.8	1.0	1.1
Gas Product, g/kg Pectin								
Gas Product Yield, wt. %	46.9	45.1	44.0	43.4	64.6	63.3	62.3	61.5
Aqueous Product Yield, wt. %	14.7	15.0	15.6	16.1	10.6	11.1	11.6	12.3
Solid Product Yield (Coke+Tar), wt. %	33.4	35.2	36.1	37.9	20.3	21.3	23.2	26.1
TOC of Aqueous Product, mg/L	560	580	605	625	410	420	450	475
Amount of Coke, g/kg Pectin	177.2	186.7	191.5	201.1	100.5	105.3	114.9	129.3

Table 43. Experimental results of Galacturonic acid SCWG at 600°C for the pressures 200, 275, 350, 425 atm without and with K₂CO₃.

Experiment No	285	286	287	288	289	290	291	292
Reaction Temperature, °C	600	600	600	600	600	600	600	600
Reaction Pressure, atm	201	281	353	424	195	281	354	425
Catalyst, 10 wt. %	-	-	-	-	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃	K ₂ CO ₃
Gas Composition, % mol								
CH ₄	10.3	12.2	13.5	15.5	13.1	14.5	16.4	17.8
H ₂	36.4	35.8	34.1	29.3	40.6	37.2	36.6	35.0
CO ₂	52.1	50.7	50.8	53.3	44.7	46.4	44.6	44.5
CO	0.4	0.3	0.2	0.1	0.6	0.5	0.3	0.2
C ₂ -C ₄	0.8	1.0	1.4	1.8	1.0	0.4	2.1	2.5
Gas Product, mol/ kg Galacturonic acid								
CH ₄	3.5	3.8	4.0	4.3	5.9	6.1	6.3	6.8
H ₂	12.2	11.4	10.2	7.8	18.2	15.5	14.0	13.4
CO ₂	17.4	16.2	15.2	14.3	20.0	19.3	17.1	16.8
CO	0.13	0.08	0.06	0.02	0.27	0.20	0.12	0.07
C ₂ -C ₄	0.29	0.35	0.46	0.5	0.4	0.6	0.8	0.9
Gas Product, g/kg Galacturonic acid								
Gas Product Yield, wt. %	70.1	67.8	65.9	64.5	88.2	87.3	85.9	84.3
Aqueous Product Yield, wt. %	6.5	7.1	7.9	8.2	3.1	3.4	3.7	3.9
Solid Product Yield (Coke+Tar), wt. %	21.6	22.8	23.7	24.4	8.1	8.8	9.4	9.9
TOC of Aqueous Product, mg/L	250	275	305	320	118	130	142	152
Amount of Coke, g/kg Galacturonic acid	114.9	120.7	125.4	129.3	43.1	46.9	49.8	52.6