



EGE ÜNİVERSİTESİ



MASTER'S THESIS

**INVESTIGATION OF THE EFFECT OF PRESSURE,
TEMPERATURE AND CATALYST ON EVOLUTION
OF HYDROGEN AND METHANE IN
SUPERCRITICAL WATER GASIFICATION OF RED
KIDNEY BEANS AND PEAS WASTES**

Doğan Emre YÜKSEL

Supervisor : Prof. Dr. Levent BALLİCE

Department of Chemical Engineering

Presentation Date : 26.10.2015

Bornova-İZMİR

2015

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

(MASTER OF SCIENCE THESIS)

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Doğan Emre YÜKSEL tarafından yüksek lisans tezi olarak sunulan “Barbunya ve Bezelye Atıklarının Kritiküstü Su Gazlaştırılmasında Basıncın, Sıcaklığın ve Katalizörün Hidrojen ve Metan Oluşumuna Etkisinin Araştırılması” 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 **26.10.2015** tarihinde yapılan tez savunma sınavında aday oybirliği/oyçokluğu ile başarılı bulunmuştur.

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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 “Barbunya ve Bezelye Atıklarının Kritiküstü Su Gazlaştırılmasında Basıncın, Sıcaklığın ve Katalizörün Hidrojen ve Metan Oluşumuna Etkisinin Araştırılması (Investigation of the Effect of Pressure, Temperature And Catalyst on Evolution of Hydrogen and Methane in Supercritical Water Gasification of Red Kidney Beans and Peas Wastes)” 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.

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İmzası

Adı-Soyadı

Doğan Emre YÜKSEL

ÖZET**BARBUNYA VE BEZELYE ATIKLARININ KRİTİKÜSTÜ SU
GAZLAŞTIRILMASINDA BASINCIN, SICAKLIĞIN VE
KATALİZÖRÜN HİDROJEN VE METAN OLUŞUMUNA
ETKİSİNİN ARAŞTIRILMASI**

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Ekim 2015, 111 sayfa

Bu çalışmada, lignoselülozik yapıdaki biyokütlelerden olan bezelye ve barbunya atıklarının, kritiküstü su gazlaştırılması (SCWG) ile hidrojen ve metan üretimi araştırılmıştır.

Değerlendirilemeyen biyokütlelerden olan bezelye ve barbunya kabukları model atık bileşik olarak seçilmiş olup 100 ml reaktör hacmine sahip çalkalamalı otoklav sisteminde deneyler gerçekleştirilmiştir. 300, 400, 500, 600°C’de katalizörsüz ve katalizör olarak Trona, Dolomit, Boraks, Sodyum Hidroksit ve Potasyum Hidroksit kullanarak denemeler yapılmıştır.

Farklı analiz teknikleri kullanılarak gaz, sıvı ve katı ürünler analiz edilmiş ve barbunya ve bezelye kabuklarının kritik üstü su gazlaştırması koşullarına etki eden parametreler hakkında yorum yapılmıştır. Gaz ürünlerde ana bileşenler CO₂, H₂ ve CH₄ olup, az miktarda CO ve C₂-C₄ hidrokarbonları da bulunmaktadır. Sıvı üründe suda çözünebilen organikler ve katı olarak da kok ve katran oluşumu gözlenmiştir. Denemeler sonucunda sıcaklık arttıkça gaz ürünün arttığı ve sıvı ürünün azaldığı görülmüştür.

Anahtar sözcükler: Kritik Üstü Su Gazlaştırması (SCWG), Barbunya ve Bezelye Atıkları, Katalizör, Hidrojen, Metan.

ABSTRACT**INVESTIGATION OF THE EFFECT OF PRESSURE,
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MSc in Chemical Eng.

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October 2015, 111 pages

In this study, hydrogen and methane production by supercritical water gasification (SCWG) of peas and red kidney beans wastes, these structure is lignocellulosic biomass, was investigated.

Peapod and Red kidney bean shells which does not be recovered were chosen as model waste compounds and the experiments were performed in 100 ml shaking autoclaves. The experiments were carried out without and with catalysts as Trona, Dolomite, Borax, KOH and NaOH.

Gas, liquid and solid products were analyzed by different techniques understand the effects of parameters on SCWG of red kidney bean shells and peapod. The main gas products were CO₂, H₂ ve CH₄, also there were trace amount of CO ve C₂-C₄ hydrocarbons. Formation of water-soluble organics, coke and tars were observed in liquid and solid products, respectively. After the experiments, increase of gas product and decrease of liquid product with increasing temperature were seen.

Keywords: Supercritical Water Gasification (SCWG), Red Kidney Beans and Peas Wastes, Catalyst, Hydrogen, Methane

ACKNOWLEDGEMENT

Firstly, I would like to express my special thanks to Prof. Dr. Mehmet Sağlam, Prof. Dr. Mithat Yüksel and my advisor Prof. Dr. Levent Ballice for the continuous support of my M.Sc. study and related research, for their patience, motivation, and immense knowledge. Their guidance helped me in all the time of research and writing of this thesis.

Secondly, I am pleased to BAP (Bilimsel Araştırma Projeleri – Scientific Research Projects, Project No: 5.101.2013.0081) for their financial support.

Also, I would like to thank all members of Chemical Technologies Laboratory Group: Dr. Tülay Güngören Madenoğlu, Gürsel Serin, Res. Asist. Nihal Üremek Cengiz, Asist. Prof. Dr Murat Sert, Res. Asist. Dilek Selvi Gökkaya. I thank all of my friends who were B.Sc. and M.Sc students, especially Özgül Kaymak and Merve Tuğçe Yaşa for their precious help. Moreover, I appreciate to Prof. Dr. Nalan Kabay for helpful advice during my academic life.

Last but not the least, I would like to thank my family: my parents and to my sister for supporting me spiritually throughout writing this thesis and my life in general.

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LIST OF SYMBOLS AND ABBREVIATIONS

<u>Symbols</u>	<u>Explanations</u>
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T	Temperature (°C)
T _c	Critical Temperature (°C)
P	Pressure (bar)
P _c	Critical Pressure (bar)

<u>Abbreviations</u>

g	gram
kg	kilogram
wt	weight
min	minute
h	hour
mL	milliliter
L	liter
GC	Gas chromatography
FID	Flame ionization dedector
TCD	Thermal conductivity dedector
GC-MS	Gas chromatography-mass spectroscopy
HPLC	High performance liquid chromatography

LIST OF SYMBOLS AND ABBREVIATIONS (CONTINUED)Abbreviations

TOC	Total organic carbon
SCW	Supercritical water
SCWG	Supercritical water gasification
SCWO	Supercritical water oxidation
RKBS	Red kidney bean shells
Mtoe	Million tonnes oil equivalents
TWh	TeraWatt hour

1. INTRODUCTION

Hydrogen is considered as clean and has high calorific value for energy and increasing its interest around the world makes it energy of future. Now, almost all produced hydrogen is observed from natural and fossil fuels via steam methane reforming (MSR) and coal gasification. These production pathways are not an environmental friendly and not economic and cause significant CO₂ emissions (Gao et al., 2009).

In this setting, biomass is a moderately expansive energy source globally which contains wood, municipal solid wastes and agricultural residues, is being examined in different countries as a possibly critical renewable source. Biomass is gotten from sun based energy and it is generally spotless contrasted with different energy sources. Biomass is thought to be CO₂ neutral as the CO₂ discharged while transformation procedures will be re-caught by the regrowth of the biomass through photosynthesis. This type of energy can be changed over to gaseous fuel through thermochemical gasification. What's more, the lower discharge of earth hazardous gasses, for example, sulfur dioxide (SO₂) and nitrogen oxides (NO_x), pending the gasification of biomass additionally assumes a positive part in decreasing worldwide acid rain development. In addition, the lower emission of environmentally detrimental gases, such as sulphur dioxide (SO₂) and nitrogen oxides (NO_x), during the gasification of biomass also plays a positive role in reducing global acid rain formation (Zhang et al., 2010; Cohce et al., 2010).

Supercritical water gasification (SCWG) is an inventive thermo-chemical strategy which can change over wet lignocellulosic biomass and organic wastes into hydrogen-rich gasses. It caught attention subsequent to being created in 1970s. It was attracted much attention after being developed in 1970s. SCWG of different sorts of biomass model compounds, genuine biomass and organic wastes were concentrated on by the scientists all around the world (Cao et al., 2011).

In SCWG, a gas blend containing H₂, CH₄, CO₂, and CO is the fundamental products, with tar and char side products also forming. Water above its critical point (T=374°C, P=22.1MPa) has thermo-physical properties that are intermediate between gas and liquid. Subsequently, there is no difference between gas stage and fluid stage because of its particular transport and dissolvability properties. In such conditions, water experiences important changes in its physical properties, containing decrement in dielectric constant, thermal conductivity, , ion

products, viscosity, and density. Supercritical water along these lines behave as a homogeneous, non-polar solvent with high diffusivity and transport properties. It can dissolve most of organic compounds and gasses, therefore organic compounds in supercritical water might readily separate to gaseous products. Thus, gasification reactions completed in the homogeneous single-stage medium offered by SCW continue quickly and create less tar and char because of the extraordinary contribution of water as both a solvent and a reactant. Likewise, this extraordinary reaction media is of significance in light of the fact that it doesn't prompt any mass transfer restriction between phases and in this manner, prompts shorter residence time and consequently to smaller reactor volumes (Letelier et al., 2010; Sricharoenchaikul, 2009; Huelsman and Savage, 2013).

In this project, red kidney beans and peas wastes as a model compound is selected. Biomass which has got less than 1 mm particle size puts in reactor being 0.1 L and having autoclave system and then reaction starts. Presence and absence of catalyst temperature experiments were done according to design of experimental plans at 300, 400, 500, 600°C. Trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$), Dolomite ($\text{CaMg}(\text{CO}_3)_2$), Borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), KOH and NaOH were used as a catalyst. As a consequence of reaction occurs some products and expected changes were observed with solid, liquid and gas analysis devices (GC, GC-MS, HPLC, TOC and TOC-SSM).

With these studies, production of hydrogen and methane from lignocellulosic biomass such as red kidney beans and peas wastes was investigated by SCWG. Turkey has got large biomass potential. In addition, this type works are very important to Turkey which is energy dependent on other country for developing own technology and accumulation of own knowledge.

2. GENERAL INFORMATION

2.1 General View of Energy in the World and in Turkey

The processes of industrialization and economic development require energy. The interest for energy is relied upon to increment at a quicker rate in up and coming years, incompletely because of the exponential development of the world's populace. Energy resources have been separated into three classes: fossil fuels, renewable sources and nuclear sources. Nuclear energy can bring about significant issues for the environment and human wellbeing; for instance, those brought about by nuclear accidents, for example, Chernobyl in 1986. Combustible fuels are the world's fundamental energy resource and are at the focal point of worldwide energy requests. On the other hand, the stores of fossil fuels are restricted, and their extensive scale utilization is connected with natural decay. Known negative impacts of utilizing fossil energizes incorporate acid rain, ozone layer consumption and worldwide environmental change. The outcome has been a fast development in the level of greenhouse gas discharges and an increment in fuel costs, which are the primary driving forces behind endeavors to use renewable energy sources (Agugliaro et al., 2013).

Worldwide Global primary energy consumption from all sources in 2008 was 514 (EJ = exajoule = 10^{18} J), with more than 80% being from fossil fuels. In any case, the world reserves of primary energy and raw materials are, clearly, restricted. Approximately, the reserves will last an additional 218 years for coal, 41 years for oil, and 63 years for natural gas, under the same old thing scenario. For this situation, totally come up short on oil and natural gas inside of the present century, in the following century not just as a source of non-renewable fossil fuels of coal is relied upon to remain. These reasons have been the world's energy mission. The renewable energy sources, for example, biomass, hydro, wind, sun based (warm and photovoltaic), geothermal, marine, and hydrogen will assume an imperative part later on. By 2040, more or less a large portion of the worldwide energy supply will originate from renewables, and electricity generation from renewables will be more than 80% of the total worldwide electricity supply (Acaroğlu and Aydoğan, 2012; Moriarty and Honnery, 2012).

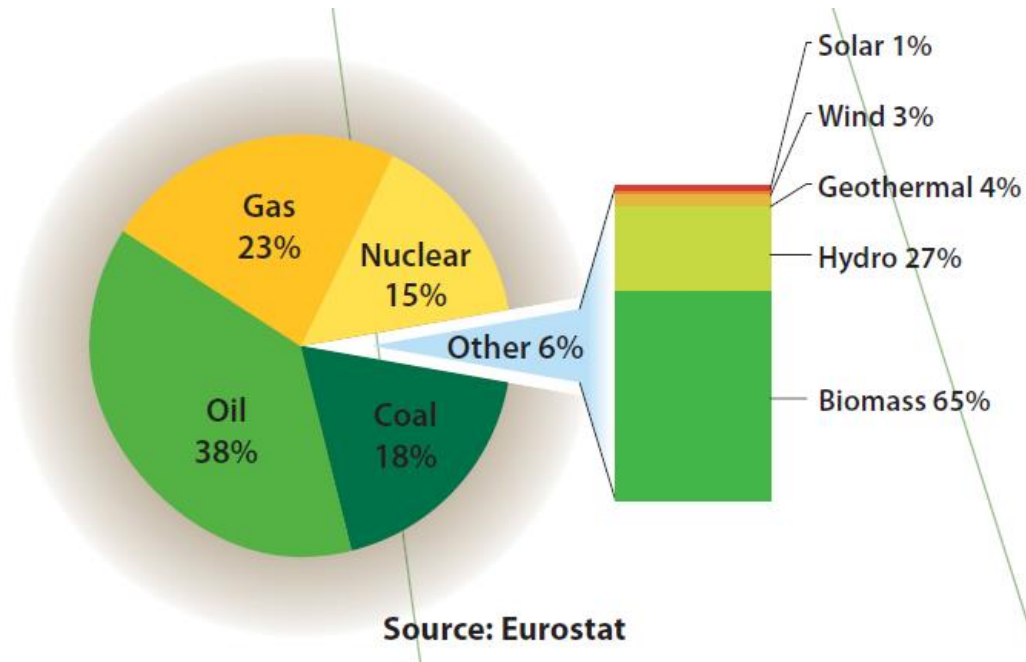


Figure 2.1.1 Breakdown of energy consumption in the EU-25 in 2002 (European Commission, 2005).

Figure 2.1.1 shows in the 25 nations of the European Union (EU), renewable energy sources gave around 6% of total energy necessities in 2002. The objective is for the renewable energy offer to achieve 12% in 2010 (European Commission, 2005).

Energy is one of Turkey's most critical improvement needs. Consequently, use of indigenous renewable energy sources is of crucial significance for Turkey to decrease its dependence on foreign energy supplies, give supply security and avoid the increment in greenhouse gas emission. Turkey's energy approach focuses to build the present offer of renewable energy from 20% to 30% in advancing years. Turkey has a very various energy sources, including hard coal, lignite, oil, hydropower, natural gas, geothermal, wood, animal and plant wastes and solar. Then again, use of these resources is not at wanted levels to supply the demand of the nation. Figure 2.1.2 demonstrates the energy demand of Turkey has been becoming more quickly than the energy generation since it is a socially and financially developing nation (Baris and Kucukali, 2012).

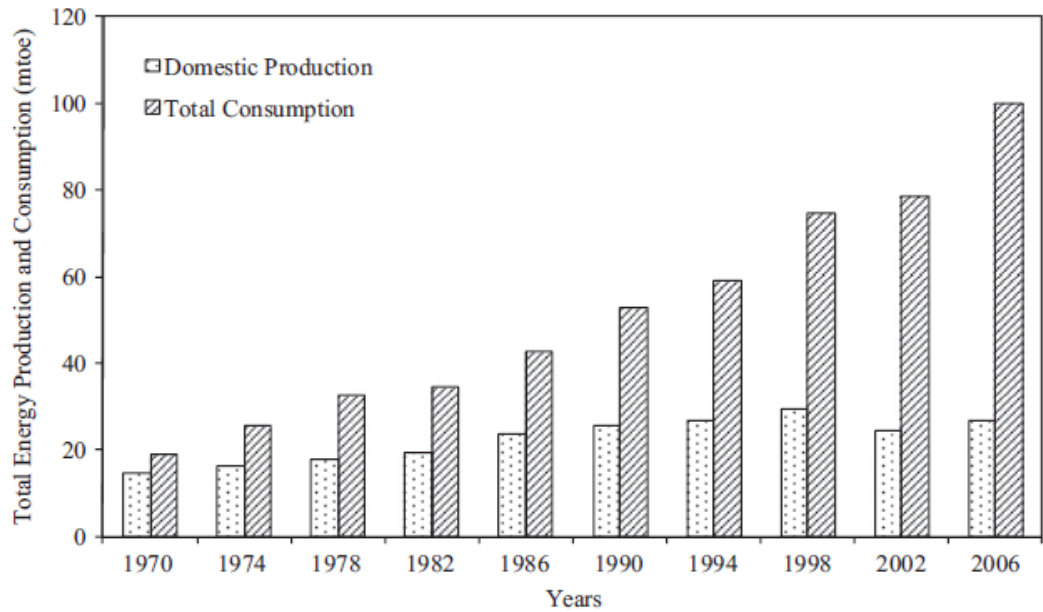


Figure 2.1.2 Tendency of total energy production and consumption of Turkey between 1970 and 2006 (Baris and Kucukali, 2012).

There is practically all sort of energy sources accessible in Turkey. On the other hand, these sources aside from lignite and water powered energy are insufficient to meet the energy necessity of the country; consequently, more than half measure of this prerequisite is met by imported energy. In Table 2.1.1, the capability of renewable energy in Turkey is given. With regard to this table, contingent upon the sun based belt on which Turkey is found, the technical solar energy potential with a measure of 6105 TWh / year is high regarding electricity generation, followed by the wind energy potential with an expected estimation of 290 TWh / year and the hydro technical potential with 216 TWh / year (Ozgur, 2008).

Table 2.1.1 Renewable energy potential of Turkey (Ozgur, 2008).

Renewable energy source	Usage kind of energy	Natural potential	Technical potential	Economic potential
Solar energy	Electrical energy (TWh/year)	977,000	6105	305
	Heat (mtoe/year)	80,000	500	25
Hydraulic energy	Electrical energy (TWh/year)	433	216	127.4
Wind energy				
Direct terrestrial	Electrical energy (TWh/year)	400	110	50
Direct maritime	Electrical energy (TWh/year)	–	180	–
Sea wave energy	Electrical energy (TWh/year)	150	18	–
Geothermal energy	Electrical energy (TWh/year)	–	–	1.4
	Heat (MW _{th})	31,500	7500	2843
Biomass energy	Fuel (classic) (mtoe/year)	30	10	7
	Fuel (modern) (mtoe/year)	90	40	25

Biomass can be utilized to meet a mixture of energy needs, including creating power, warming homes, fueling vehicles and giving process heat for industrial facilities. Table 2.1.2 demonstrates Turkey's yearly biomass energy potential. Present and arranged biomass energy production in Turkey is given in Table 2.1.3 (Demirbas, 2008).

Table 2.1.2 Turkey's yearly biomass energy potential (Demirbas, 2008).

Type of biomass	Annual potential (million tons)	Energy potential (Mtoe) ^a
Annual crops	55	14.9
Perennial crops	16	4.1
Forest residues	18	5.4
Residues from agro industry	10	3.0
Residues from wood industry	6	1.8
Animal wastes	7	1.5
Other	5	1.3
Total	117	32.0

Table 2.1.3 Present and planned biomass energy production (ktoe) in Turkey (Demirbas, 2008).

Years	2003	2005	2010	2015	2020	2025	2030
Classic biomass	6613	6495	5754	4790	4000	3345	3310
Modern biomass	658	766	1660	2430	3520	4465	4895
Total biomass	7271	7261	7414	7320	7520	7810	8205

2.2 Biomass as a Renewable Source

Biomass refers to the organic, biodegradable fraction of products, waste and residues from agriculture (including vegetable and animal matter), forestry and related industries, as well as the biodegradable fraction of industrial and municipal waste. Although carbon dioxide is emitted when biomass is burned, it is considered a clean source of energy because there is no net release of CO₂ when the cycle of growth and harvest is sustained as a result of the natural carbon cycle, i.e. photosynthesis in plants. For the same reason, biomass is also considered a renewable source of energy.

The main benefits of biomass over conventional fuels are summarized below:

- Renewable and recyclable energy source (“stored solar energy”)
- Widespread availability in Europe and abroad
- Decreased depend on imported energy sources
- Less waste directed to landfills
- Low fuel cost compared to fossil fuels
- Can be stored and used on demand
- Stable employment opportunities, especially in rural areas
- Good opportunities for technology exports
- Reduced CO₂ and other emissions
- Source of many business opportunities
- Contribution to a balanced growth of agriculture (SRS NET&EEE, 2008).

Biomass comes in various forms each of which has specific properties, uses and advantages. The main sources are wood from conventional and short-rotation forestry, other energy crops, residues from forestry and agricultural production, and by-products and wastes from industrial and municipal processes (Table 2.2.1). The energy that can be obtained from a particular resource depends on its chemical composition and moisture content (Table 2.2.2) (European Commission, 2005).

Table 2.2.1 Examples of biomass resources (European Commission, 2005).

Category	Examples
Dedicated plantations	Short-rotation forestry (eucalyptus, willow) Perennial crops (miscanthus) Arable crops (rapeseed, sugarcane, sugarbeet)
Residues	Wood from forestry thinning Wood felling residues Straw from cereals Other residues from food and industrial crops (sugarcane, tea, coffee, rubber trees, oil and coconut palms)
By-products and wastes	Sawmill waste Manure Sewage sludge Organic fraction of municipal waste Used vegetable oils and fats

Table 2.2.2 Heating values of various types of biomass (European Commission, 2005).

Biomass type	Higher heating value in GJ/tonne
Dry lignocellulosic	18
Wet cellulosic	9
Oils and fats	36
Ethanol	26

Table 2.2.3 gives an idea of the crop an energy yields that can be expected from different types of woody and nonwood energy crops. Ranges of yield data are given because actual yields depend on land type and climate. From the information in the table it can be seen that to achieve the 1.2 EJ a year solid biomass mentioned earlier in 2010 would require something like 6.3 million hectares land. This is little more than the 5.7 million hectares set aside in the EU in 2001. In that year, only 0.9 million hectares of the set aside were seperated to non-food crops. It should not be difficult to increase that figure in the future (European Commission, 2005).

Table 2.2.3 Crop and energy yields from some energy crops (European Commission, 2005).

Crop	Yield (dry tonnes/hectare/year)	Energy yield (GJ/hectare/year)
Woody crops		
Wood	1-4	30-80
Tropical plantations (with no fertiliser and irrigation)	2-10	30-180
Tropical plantations (with fertiliser and irrigation)	20-30	340-550
Short rotation forestry (willow, poplar)	10-15	180-260
Non-woody crops		
Miscanthus/switchgrass	10-15	180-260
Sugarcane	15-20	400-500
Sugarbeet	10-21	30-200
Rapeseed	4-10	50-170

2.3 Production Ways of Hydrogen Production from Biomass

Biomass can be changed over into helpful types of energy items utilizing various distinctive procedures. Variables that impact the decision of procedure are the sort and amount of biomass feedstock. There are two courses for biomass change into hydrogen-rich gas, in particular (i) Thermo-chemical transformation, and (ii) Bio-chemical/biological transformation (Kalinci et al., 2009). Figure 2.3.1 presents these conversion ways in a clearer way.

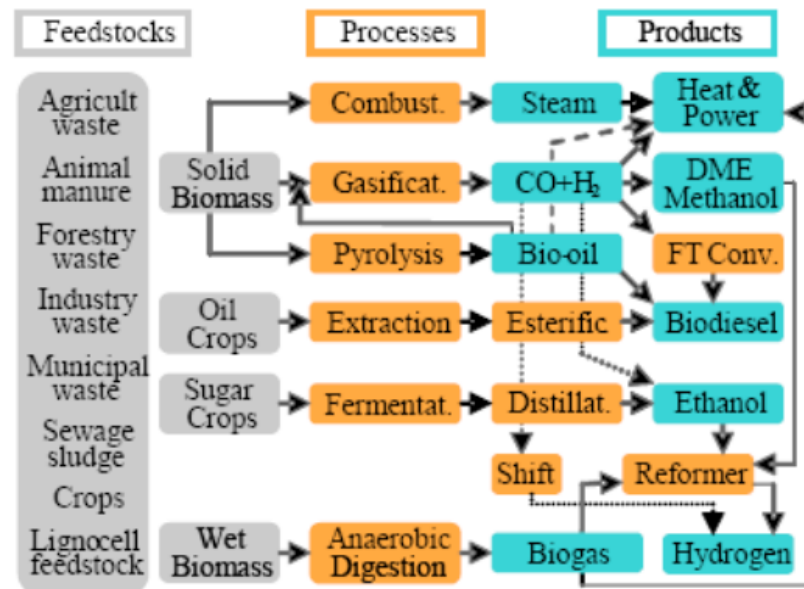


Figure 2.3.1 Biomass conversion paths (IEA, 2007).

Within the thermochemical processes the main ones that can be mentioned for general treatment of biomass are: combustion, gasification, liquefaction and pyrolysis. Due to limitations in efficiency and operation, both combustion and liquefaction are not well fitting with the production of hydrogen. So the main thermochemical processes that are being used and investigated regarding hydrogen production are pyrolysis and gasification processes. A brief introduction to both of them is presented as follows.

Pyrolysis is a thermal process in which biomass is heated at a temperature ranging from 625 to 800K in the absence of oxygen and air. During this process, the biomass breaks into different phase state products coexisting solids, liquids and gasses at the end of the process. The ratio of products is heavily depending on the velocity of the process. The slower the speed of the process the more solid products ratio. Conventional pyrolysis (slow) is associated with high charcoal

product, so the interest, when focusing to hydrogen production, is on fast processes. Those are called fast (or flash) pyrolysis, where biomass is treated in time ranges of the order of a few seconds (or even under 1 second, in flash pyrolysis), and where the main products are in liquid and/or gas phase (HYRREG, 2013).

Gasification change over fossil or nonfossil fuels (solid, liquid, or gaseous) into useful gases and chemicals. It need a medium for reaction, which can be gas or supercritical water (not to be mistaken for common water at subcritical condition). Gaseous mediums incorporate air, oxygen, subcritical steam, or a blend of these. Currently, gasification of fossil fuels is more basic than that of nonfossil fuels like biomass for generation of synthetic gases. It basically changes over a potential fuel starting with one structure then onto the next. Gasification of biomass likewise includes eliminate of oxygen from the fuel to expand its energy concentration. Case in point, a typical biomass has around 40 to 60% oxygen by weight, yet a helpful fuel gas contains just a little rate of oxygen. The oxygen is purged from the biomass by either dehydration or decarboxylation. Biomass gasification into CO and H₂ gives a good base to creation of fluid transportation fuels, for example, gasoline, and synthetic chemicals, for example, methanol. It additionally generates methane, which can be burned directly for energy creation. Gasification is done by and large in one of the three noteworthy sorts of gasifiers:

- Moving bed (also called fixed bed)
- Fluidized bed
- Entrained flow (Basu, 2010).

Another technique for biomass-based hydrogen is biological conversions. These are abridged as fermentative hydrogen creation, photosynthesis procedure and hydrogen generation by biological water gas shift reaction. All procedures rely on hydrogen production enzymes.

Biohydrogen creation can be acknowledged by anaerobic (dark fermentation) and photoheterotrophic (light fermentation) microorganisms utilizing carbohydrate rich biomass as a renewable source. The primary step is the acid or enzymatic hydrolysis of biomass to very concentrated sugar solution which is further fermented by anaerobic life forms to deliver volatile fatty acids, hydrogen and CO₂. The organic acids are further fermented by the photo-heterotrophic bacteria (*Rhodobacter* sp) to create CO₂ and H₂ which is known as

the light fermentation. Joined use of dark and photo fermentations was accounted for to enhance the yield of hydrogen generation from carbohydrates.

Numerous phototropic life forms, for example, purple bacteria, green bacteria, Cyanobacteria and a few algae can be utilized to create hydrogen with the guide of solar energy. Microalgae, for example, green algae and Cyanobacteria, absorb light energy and create electrons. The electrons are then exchanged to ferredoxin (FD) utilizing the solar energy consumed by photosystem. Be that as it may, the mechanism fluctuates organism to organism yet the principle steps are alike.

The Biological water gas shift reaction a moderately new system for hydrogen creation. Some bacteria (certain photo-heterotrophic bacteria), for example, *Rubrivivax gelatinosus*, are equipped for performing water gas shift reaction at ambient temperature and atmospheric pressure. Such microscopic organisms are able to survive in the dark by utilizing CO as the sole carbon source to create adenosine triphosphate (ATP) coupling the oxidation of CO with the reduction of H^+ to H_2 (Kalinci et al., 2009).

2.4 Supercritical Water Gasification

Supercritical water gasification is a kind of biomass gasification where supercritical water (374°C and 22.1 MPa) is used as the medium. Therefore, the fundamental contrast between SCWG and other thermochemical gasification methods is identified with their gasification medium for example, supercritical water or inert gas and/or steam. Supercritical water has a double part as a reactant and medium in the gasification of biomass. The likelihood of production of H^+ and OH^- particles at high density is greater at supercritical conditions making an environment for hydrolysis and pyrolysis reaction. Around the supercritical point, water is capable of generating ions which assists in degradation of biomass components. Lignocellulosic biomass which comprises of cellulose and hemicellulose gets dissolved at high temperature and pressure in SCW. These particles further breakdown to basic sugars which are gasified by rising the reaction temperature and pressure. Lignin in biomass turns to phenolic mixes which are further changed to basic gasses, for example, H_2 , CO, CO_2 and CH_4 (Reddy et al., 2014).

The benefits of SCWG are as per the following:

- SCWG has been exhibited to change over wet biomass to high yields of gases including hydrogen and methane (Guan et al., 2012).
- Decomposition of biomass in supercritical water is quick, high solubility of the intermediates in SCW restrains tar and coke development and high product yields are acquired at moderately low temperature (Markočič et al., 2013).
- SCW indicates a moderately high heat capacity that prompted efficient heat transfer (Furusawa et al., 2007).
- Wet biomass does not should be dried, which is cost-effective contrasted with conventional gasification processes.
- CO₂ has high solubility in high pressurized water at room temperature, therefore it can be effectively separated from H₂.
- Gaseous product is clean and the effluent can be utilized as fertilizer (Baris and Kucukali, 2012).

SCWG is an innovation in the early stages of technical improvement. A better comprehension of the fundamental phenomena is crucial for a satisfactory SCWG reactor-and process design. For maximizing conversion and to enhance the gas yield and composition, explore on the key parameters impacting the general process effectiveness is of incredible significance. Figure 2.4.1 demonstrates a schematic of a continuous SCWG reactor. The set up comprises of a feed storage for the wet biomass, a pump for pumping the slurry at supercritical pressure, the SCWG reactor and a heat exchanger to warm the reactants and cool the hot product gasses. After the heat exchanger the hot product gasses are cooled further utilizing a cooling system and afterward the two stage product stream is isolated utilizing a high pressure and low pressure separator (Withag et al., 2012).

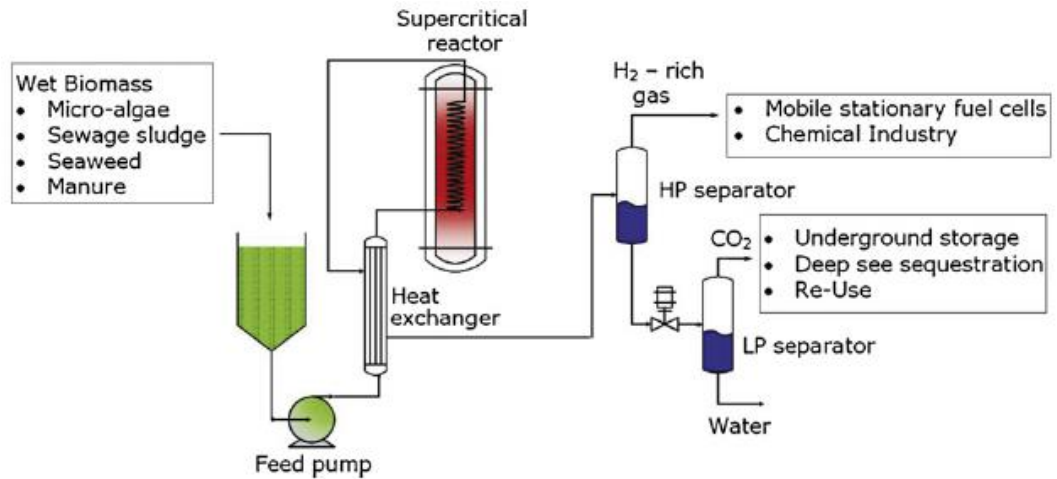


Figure 2.4.1 Representation of the full chain of biomass gasification in supercritical water (Withag et al., 2012).

2.5 Properties of Supercritical Water

The critical temperature (374°C) and critical pressure (22.1 MPa) of water called supercritical water and water has smaller value of the critical temperature and above the vapor pressure at that temperature called subcritical water; and, above the critical temperature and below the critical pressure is high-pressure superheated steam. The temperature and pressure districts in which every sort of water exists are demonstrated in the phase graph of water in Figure 2.5.1 (Okajima and Sako, 2014).

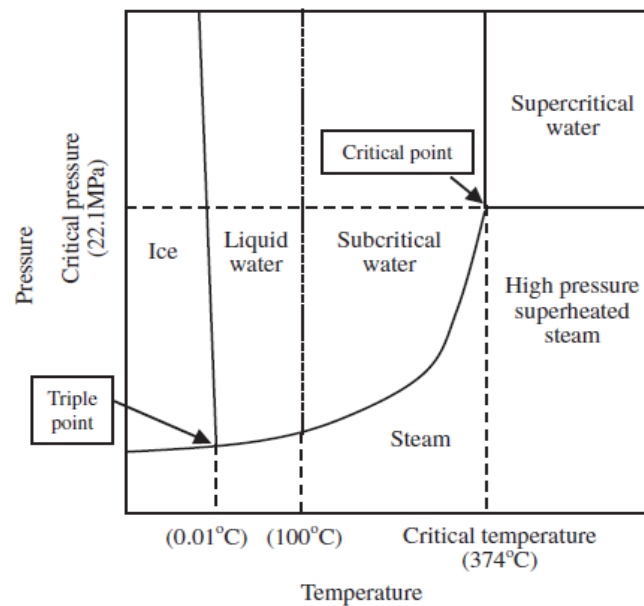


Figure 2.5.1 Phase diagram of water (Okajima and Sako, 2014).

Water is named in common may not be suitable to SCW out of its chemical formula, H_2O , because above the critical temperature SCW behaves like either water or steam. It has a density like water but a diffusivity like steam. Table 2.5.1 looks at the properties of subcritical water and steam with those of SCW, showing that SCW's properties are middle between the liquid and vaporous conditions of water in subcritical pressure; explanation of each is demonstrated the table (Basu, 2010).

Table 2.5.1 Properties of supercritical and subcritical water (Basu, 2010).

Property	Subcritical Water	Supercritical Water	Supercritical CO_2	Subcritical Steam
Temperature ($^{\circ}C$)	25	400	55	150
Pressure (MPa)	0.1	30	28	0.1
Density, kg/m^3	997*	358*	835	0.52*
Dynamic viscosity, μ (kg/m.s)	890.8×10^{-6}	43.83×10^{-6} *	0.702×10^{-6}	14.19×10^{-6} *
Diffusivity of small particles (m^2/s)	$\sim 1.0 \times 10^{-9}$ **	$\sim 1.0 \times 10^{-8}$ **		$\sim 1.0 \times 10^{-5}$ **
Dielectric constant***	78.46	5.91		1.0
Thermal conductivity, λ (w/m.k)	607×10^{-3} *	330×10^{-3} *		28.8×10^{-3} *
Prandtl number, $C_p\mu/\lambda$	6.13	3.33		0.97

The critical point denote a critical change in the thermophysical properties of water (Figure 2.5.2). The specific heat near the critical temperature increase suddenly, after this point there is a similar drop. The thermal conductivity of water falls from 0.330 W/m.K at 400 $^{\circ}C$ to 0.176 W/m.K at 425 $^{\circ}C$. The decrement in molecular viscosity is also important, while the viscosity begins increasing with temperature above the critical point. Over this critical point, water encounters a sensational change in its dissolvable nature principally in view of its loss of hydrogen bonding. The dielectric constant of the water falls from an estimation of around 80 in the ambient condition to around 5 at the critical point. This alteration makes the water from an exceptionally polar solvent at an ambient condition to a nonpolar solvent, similar to benzene, in a supercritical condition.

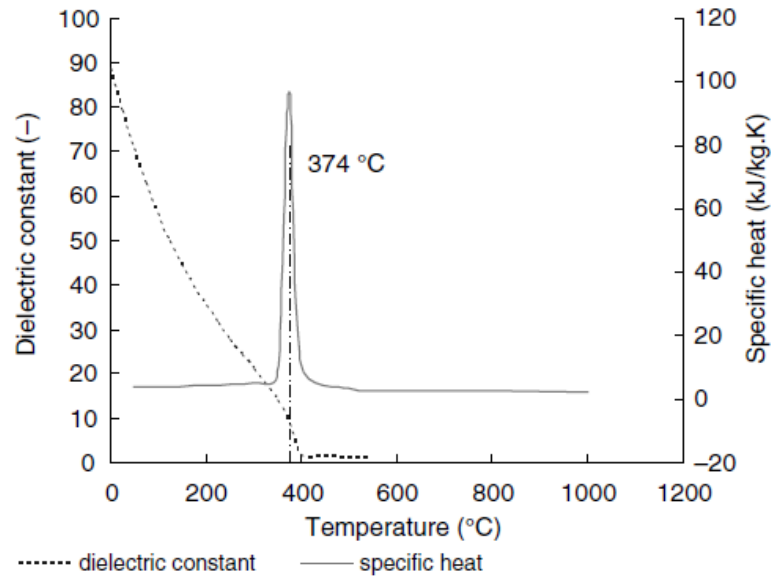


Figure 2.5.2 Specific heat and dielectric constant of water (Basu, 2010).

Density change of supercritical water with its pseudo-critical temperature is much more moderate, yet. To illustrate, it decreases from about 1000 to 200 kg/m³ at 25 MPa while the state of water changes from liquidlike to vaporlike. At subcritical pressure, however, there is an order of magnitude drop in density when the water goes past its saturation temperature. For instance, at 0.1 MPa or 1 atm of pressure, the density drop from 1000 to 0.52 kg/m³ when the temperature rise from 25 to 150 °C (see Table 2.5.1).

The most essential element of supercritical water is that we can "manipulate" and control its properties around its basic point just by modifying the temperature and pressure. Supercritical water has various extraordinary properties that separate it from common water. Some of those properties pertinent to gasification are as per the following:

- The solvent characteristic of water can be changed dramatically close or over its critical point as a function of temperature and pressure.
- Subcritical water is polar, however supercritical water is nonpolar in view of its low dielectric constant. Therefore, it is a good solvent for nonpolar organic compounds however a poor one for highly polar inorganic salts. SCW is able to be a dissolver for gases, lignin, and starches, which show low dissolvability in subcritical water. Great miscibility of intermediate solid organic compounds and also vaporous products in liquid SCW

permits single-phase chemical reactions while gasification, elevating the interphase barrier of mass transfer.

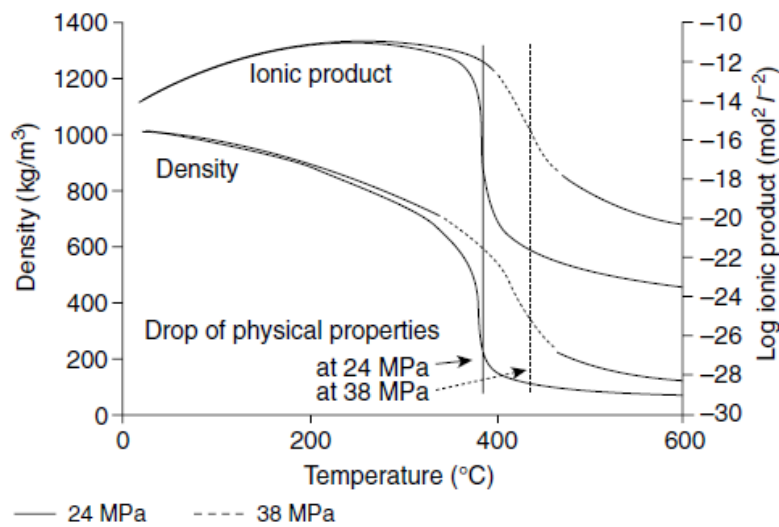


Figure 2.5.3 Density and ion product of water depend on temperature at 24 and 38 MPa (Basu, 2010).

- SCW has a high density contrasted with subcritical steam with similar temperature. This property supports the forward reaction between cellulose and water to generate hydrogen. This feature favors the forward reaction between cellulose and water to produce hydrogen.
- Ion products of water which is near critical point ($[H^+][OH^-] \sim 10^{-11} \text{ (mol/l)}^2$) are higher for water than subcritical state at ambient conditions ($\sim 10^{-14} \text{ (mol/l)}^2$) (Figure 2.5.3). Because of this high $[H^+]$ and $[OH^-]$ ion, the water can be an effective medium for acid- or base-catalyzed organic reactions. Above the critical point, even though, the ion product decreases rapidly ($\sim 10^{-24} \text{ (mol/l)}^2$ at 24 MPa), and the water is a bad medium for ionic reactions.
- Most ionic substances, for example, inorganic salts, are dissolvable in subcritical water, however almost insoluble under similar conditions of SCW gasifiers. As the temperature increase past the critical point, the density and in addition the ionic product declines (Figure 2.5.3). In this way, highly soluble normal salt (NaCl) gets to be insoluble at higher temperatures over the critical point. This tunable solubility property of SCW makes it moderately simple to separate the salts and the gasses from the product blend in a SCW gasifier.

- Gasses, for example, oxygen and carbon dioxide, are very miscible in SCW, permitting homogeneous reactions with organic molecules either for oxidation or for gasification. This property makes SCW a perfect medium for suppression of unsafe chemical waste through SCWO.
- SCW has perfect transport properties. Its density is lower than that of subcritical water yet much higher than that of subcritical steam. This, alongside different properties like low viscosity, low surface tension (surface tension of water declines from 7.2×10^{-2} at 25 °C to 0.07 at 373 °C), and high diffusivity extraordinarily helps the SCW's great transport property, which permits it to effortlessly enter the pores of biomass for effective and fast reactions.
- Decreased hydrogen bonding is another property of SCW. The high temperature and pressure break the hydrogen-bonded system of water molecules (Basu, 2010).

3. LITERATURE REVIEW

There exist a few energy production processes available for the production of hydrogen (or other products) from biomass. Those can be divided in two main groups, regarding on the mechanisms behind the transformations: Thermochemical and biological. In addition, each of them consists of sub-divided groups. These are;

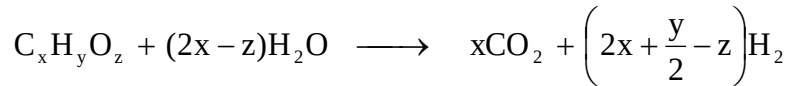
- Thermochemical processes
 - Pyrolysis
 - Gasification (in the presence of air or O₂ and/or steam)
 - Super critical water gasification (SCWG)
- Biochemical/biological processes
 - Biophotolysis
 - Photo fermentation
 - Dark fermentation
 - Biological water-gas shift reaction (HYYREG, 2013).

The essential properties of supercritical water ($T > 374^{\circ}\text{C}$ and $P > 22.1 \text{ MPa}$), for example density, viscosity, dielectric constant, and dipole moment, are very different from those of steam or liquid water. Water's dielectric constant declined sharply from normal point about 80 to 5 due to decreasing and weakens hydrogen bonds at the critical point. This range in dielectric constant of water may be concluded big change in solving capacity. Dielectric constant of supercritical water is getting to be like common organic compounds so the great dissolvability causes it a solvent for nonpolar organic compounds. Conversely, dissolving limit for high polar inorganic mixes drops drastically, which provide sort dissolved organic compounds out of water (Ortiz et al., 2013; Madenoğlu et al., 2013; Guo et al., 2010).

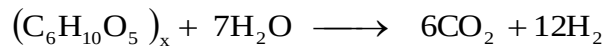
Biomass has got 4 main components as cellulose, hemicelluloses, lignin and extractives (inorganic salts). Their species and amounts changes according to plant species, part of plants and plants age. In general, plants has got between 30-50% cellulose, 20-40% hemicellulose, lignin 15-25% and 1% in the inorganic salts.

Cellulose linked each other with oxygen bridges by numerous β -D-Glucose molecules is polysaccharide. However, the structure of hemicelluloses being a

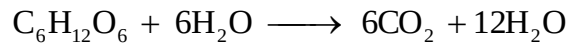
polysaccharide has 6 carbon hexoses (mannose, galactose, fructose, and leviloz), 5 carbons pentoses (xylose and arabinose) and pectin (poligalakto-üranoik acid methyl esters). Hemicellulose, alkali-soluble portion of the plant may be called cold. According to Freudenberg (1966), lignin consisted building blocks as coniferyl alcohol, sinapil alcohol and p-cuman alcohol and its aromatic character is very complex structure. General molecular formula of organic content of biomass is shown as $C_xH_yO_z$ and it is written by the following stoichiometric equation for the reaction of SCWG.



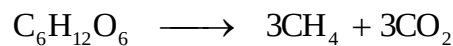
For one of the main components of cellulose:



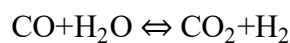
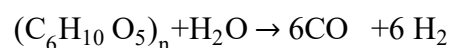
The reaction can be written. When cellulose hydrolyzes at SCW condition, glucose/fructose occurs and their reaction is following;

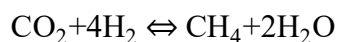
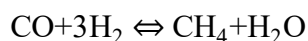


Gasification starts about 250°C because biomass and similar wastes' reactivity is very high in water at high pressure value. But, according to following reaction methane instead of hydrogen occurs at lower temperature.



At lower temperature mostly CH_4 , at higher temperature mostly H_2 occurs. Gas, the main products, but also in comparison with the normal processes of gasification or reforming consists of very low amounts of carbon monoxide. However, at above the critical temperature of water, the formation of carbon monoxide is reduced. CO converts to CO_2 and H_2 or CH_4 according to water-gas shift reaction. Moreover, according to other reaction mechanism methane can occur.





Hence, at SCWG lots of reactions becomes with an order. Gas included high amount of H_2 and CH_4 not only depended on temperature and pressure, but also catalyst and composition of biomass.

Azadi et al. investigated (2012) the catalytic activity and hydrogen selectivity of $\text{Ni}/\alpha\text{-Al}_2\text{O}_3$, $\text{Ni}/\text{hydrotalcite}$, Raney nickel, Ru/C and $\text{Ru}/\gamma\text{-Al}_2\text{O}_3$ catalysts for hydrothermal hydrogen production from lignocellulosic biomass. The feedstocks involved glucose, cellulose, fructose, xylan, pulp, lignin and bark. A batch reactor which was fed with 2 wt% concentration was used at 380°C during the experiments. The gasification of glucose, fructose, cellulose, xylan and pulp resulted in equivalent gas yields ($\pm 10\%$ at 60 min), but lignin was actually harder to gasify. Catalyst type influenced both the gasification yield and the product distribution for a given feedstock. $\text{Ni}/\alpha\text{-Al}_2\text{O}_3$ and $\text{Ni}/\text{hydrotalcite}$ catalysts were very active for the gasification of carbohydrates. Also, hydrogen selectivity of them when compared to Raney nickel, Ru/C and $\text{Ru}/\gamma\text{-Al}_2\text{O}_3$ was better. Use of Raney nickel, Ru/C and $\text{Ru}/\gamma\text{-Al}_2\text{O}_3$ caused high methane yields.

Yamaguchi et al. (2009) produced hydrogen and methane from lignin in supercritical conditions of water using various supported metal catalysts in a batch reactor. Comparison of catalysts for the lignin gasification was that: $\text{Ru}/\text{C} > \text{Rh}/\text{C} > \text{Pt}/\text{C} > \text{Pd}/\text{C} > \text{Ni}/\text{C}$. Comparison of hydrogen production was that: $\text{Pd}/\text{C} > \text{Ru}/\text{C} > \text{Pt}/\text{C} > \text{Rh}/\text{C} > \text{Ni}/\text{C}$. For lignin gasification, titania and activated carbon as supports metal catalysts behaved as stably in supercritical water. Shorter reaction time and higher reaction temperature provided to increase hydrogen percentage of gaseous products from lignin.

Sricharoenchaikul (2009) examined supercritical water gasification of black liquor (waste pulping chemicals). Suitable reaction parameters, contain pressure, temperature, feed concentration, and reaction time, to find the highest conversion and energy efficiency were researched. It was found that pressure is insignificant on gas product distribution and carbon conversion. Product gas including H_2 , CO , CH_4 , and C_2H_x increased sharply with increasing temperature and residence time. Higher carbon conversion and energy ratio were found with more diluted solution,

however energy content in the resultant product gas was lower for more concentrated solution.

In 2002, Watanabe et al. reported hydrogen production using glucose and cellulose and ZrO_2 catalyst in supercritical water (673–713 K and 30–35 MPa) with batch reactor. The experiments were carried out with alkali (NaOH) and without catalyst at the same conditions to compare. The yield of hydrogen with zirconia was nearly two times more than without catalyst for all feed (glucose and cellulose).

In the last two decades, there are many detailed studies on SCWG of some organic compounds for hydrogen producing where Forschungszentrum Karlsruhe in Germany, U.S. Pacific Northwest Laboratory (PNL), National Institute for Resources and Environment (NIRE) in Japan, Hawaii Natural Energy Institute (HNEI) and other research centers. SCWG studies in literature mainly deal with gasification of model compounds (cellulose, glucose, xylan and lignin) and real biomass to investigate chemistry of biomass transformation to decomposed products and intermediates. The effects of different catalysts, temperatures and pressure on gasification of biomass have been investigated in these studies (Madenoglu et al., 2012).

At NIRE the conversion of cellulose was examined in autoclaves with residence times of up to 1 h and with range of 200–400°C and 80–180 bar. It was found that sodium carbonate as a catalyst prevented the formation of char and oil on the other hand mainly water soluble products were produced. CH_4 and CO_2 were occurred as main products in the gas phase at 400°C with Ni catalysts (Schmieder et al., 2000).

Elliott and co-workers, from PNL (Pacific Northwest Laboratory), performed a lot of studies on biomass gasification in a high pressure with water. Nickel catalysts were used for organic wastes gasification in sub- and SCW using a batch reactor for 1–2 h running time with temperature at 623 K and pressure at 20 MPa. It was found that CH_4 -rich gas was obtained (Guo et al., 2007).

The experiments of supercritical water gasification in HNEI were performed at 600°C, 34.5 MPa, using activated carbon or charcoal as catalysts. Several feedstock, for example glucose, sawdust, and sewage sludge, were used in this study. The gasification efficiency were found approximately 100%. Liquid

effluent from the reactor can be recycled into the reactor. The effects of temperature, pressure, weight hourly space velocity, catalyst, resident time on reaction rate were studied. The gasification efficiency and product gas composition were shown in the study (Hao et al., 2003).

Research groups of the Karlsruhe Research Center, Germany, concentrated supercritical gasification of biomass lack of heterogeneous catalysts. Additionally, at the Karlsruhe Research Center, impact of different ingredients of biomass on the gasification process is examined. A fundamental result is that the alkali salts in the biomass raise the hydrogen yield (Kruse, 2009).

Yoshida and Matsumura (2001) examined the gasification of cellulose, xylan as a model material for hemicellulose, and lignin mixtures in supercritical water at 623 K and 25 MPa. A decrement of gas production was found for the mixtures including lignin. The reaction of intermediates from cellulose and xylan with lignin concluded in a reduction of H₂ production.

Cellulose and hemicellulose can hydrolyze quickly to monosaccharides which are glucose, xylose, mannose, arabinose, galactose, fructose in hydrothermal conditions. In ionic-dominated environment, these sugars dehydrated to furan type compounds such as 5-hydroxymethyl furfural (5-HMF), 5-methyl furfural (5-MF), and furfural which can forward hydrolysed and turn to carboxylic acids, alcohols, phenols, aldehydes and ketones. Lignin, because of the most resistant component of biomass to gasify, is able to hydrolyse to p-coumaryl, coniferyl or sinapyl alcohols which are produced syringols, guaiacols, catechols, phenols and cresols. Dehydration and dehydrogenation of these phenolic compounds prompts development of coke and tars. Primary degradation products of lignin are furfural and phenols that converted into gaseous products but much slower than small aliphatic hydrocarbons. Hydration of intermediate aqueous products with natural mineral catalysts provides formation of mainly carbon dioxide, carbon monoxide and small amount of hydrogen at sub-critical conditions of water (Madenoglu et al., 2014).

Spritzer and Hong have calculated approximately the SCWG production cost of hydrogen as US\$3/GJ (US\$0.35/kg) (Ni et al., 2006).

4. MATERIAL AND METHOD

4.1 Material

In this study, peapod and red kidney bean shells was used as waste biomass feedstock. First of all, feedstock was dried at room temperature and then biomass samples were grounded in a crush mill until the particle size of biomass reached below 1 mm. Elemental analysis of peapod and red kidney bean shells was performed using an elemental analyzer (CHNS-932 by Leco, MI-USA). Proximate and ultimate analysis of biomass sample is given in Table 3.1.1. Cellulose, hemicelluloses and lignin content of biomass was analyzed by method of Van Soest (Goering, H.K., and Van Soest, P.J., 1970), and the results are presented in Table 4.1.2.

Table 4.1.1 Proximate and ultimate analysis Peapod and RKBS.

<i>Proximate analysis (wt %)</i>	PEAPOD	RKBS
Moisture	10.07	7.60
Ash	5.44	6.82
<i>Ultimate analysis (dry, wt %)</i>		
C	42.30	39.01
H	6.10	5.81
N	2.06	0.87
S	0.21	0.08
O (from difference)	50.67	54.23

Table 4.1.2 The composition of Peapod and RKBS.

<i>Components (daf, wt%)</i>	PEAPOD	RKBS
Cellulose	19.71	44.33
Lignin	5.80	5.63
Hemicellulose	15.53	17.39
Extractives	56.30	29.65

Trona $[\text{Na}_3(\text{CO}_3)(\text{HCO}_3) \cdot 2\text{H}_2\text{O}]$, Dolomite $[\text{CaMg}(\text{CO}_3)_2]$, Borax $[\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}]$ were mineral catalysts those used in the experimental studies. Trona, hydrated sodium bicarbonate carbonate is an evaporate mineral (Figure 4.1.1.a). It is mined as the primary source of sodium carbonate; it has replaced the Solvay process used in most of the world for sodium carbonate production. The Trona near Green River, Wyoming is the largest known deposit in the world, where the trona was deposited in a lake during the Paleogene period. Trona has also been mined at Lake Magadi in the Rift Valley in Kenya for nearly 100 years, and occurs in ‘salt’ pans in the Etosha National Park in Namibia. 92 % of trona found in USA and 3 % in Turkey.

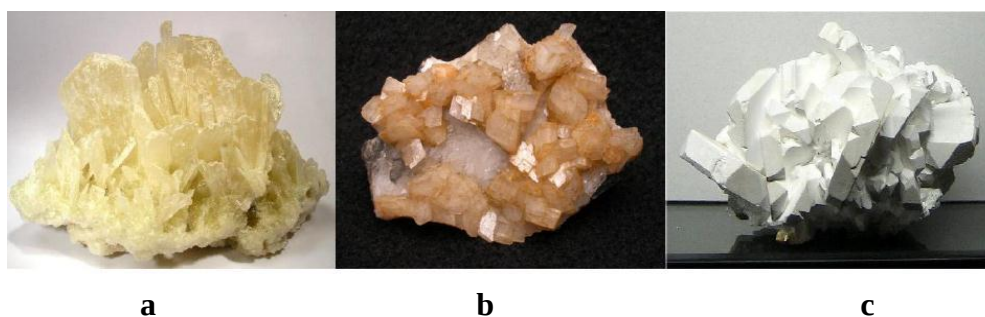


Figure 4.1.1 Trona (a), Dolomite (b), and Borax (c) mineral catalysts.

Borax, also known as sodium borate, sodium tetraborate, or disodium tetraborate, (Figure 4.1.1.c) is an important boron compound, a mineral, and a salt of boric acid. Powdered borax is white, consisting of soft colorless crystals that dissolve easily in water. It was first discovered in dry lake beds in Tibet and was imported via the Silk Road to Arabia. Borax first came into common use in the late 19th century when Francis Marion Smith's Pacific Coast Borax Company began to market and popularize a large variety of applications under the famous 20 Mule Team Borax trademark, named for the method by which borax was originally hauled out of the California and Nevada deserts in large enough quantities to make it cheap and commonly available.

Dolomite is an important sedimentary and metamorphic mineral (Figure 4.1.1.b) found as the principal mineral in dolostones and metadolostones, and as an important mineral in limestones and marbles where calcite is the principal mineral present. Also found as a hydrothermal vein mineral, forming crystals in cavities; and found in serpentinites and similar rocks. It dissolves very slowly in cold acids. Powder form of dolomite readily dissolves in warm acids with effervescence.

Potassium hydroxide (KOH) and Sodium hydroxide (NaOH) were alkali catalysts which used in this study. Potassium hydroxide is an inorganic compound and is commonly called caustic potash. KOH is highly basic, forming strongly alkaline solutions in water and other polar solvents. These solutions are capable of deprotonating many acids, even weak ones. Sodium hydroxide, also known as lye and caustic soda, is an also inorganic compound. It is a white solid and highly caustic metallic base and alkali salt which is available in pellets, flakes, granules, and as prepared solutions at a number of different concentrations.

4.2 Method

4.2.1 Experimental system

Experiments were performed with SS 316, batch autoclave. The autoclaves had 100 cm³ internal volume. There were a rotating shaker with an eccentric and a PID temperature controller in the reaction system. Diagram and Picture of the reactor are presented in Figure 4.2.1.1 and Figure 4.2.1.2, respectively.

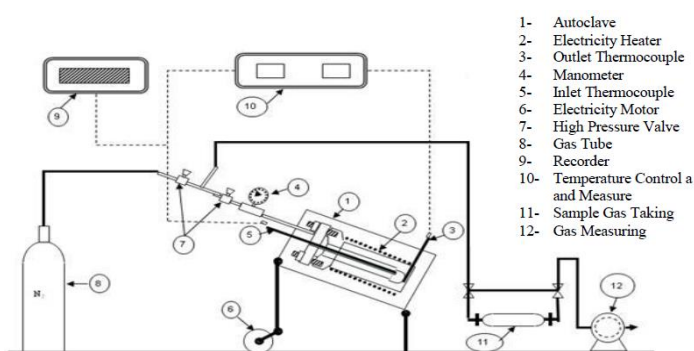


Figure 4.2.1.1 Batch autoclave system.



Figure 4.2.1.2 Schematic view of batch autoclaves and their auxiliaries.

The air was removed from the system with an inert gas stream (nitrogen) later than putting the 1.2 g of peapod or RKBS and 15 ml water into the autoclave. Desired temperature was reached with heating the internal temperature of reactor with 6 K min^{-1} and held at this temperature for 1 h. The experiments were carried out at 300°C , 400°C , 500°C , 600°C with and without 10 wt % catalyst. In catalytic tests, 0.12g catalyst was dissolved in the water which would be used except Dolomite catalyst.

Toward the end of every run, the reactor was cooled to ambient temperature quickly. The pressure of the collected gaseous product was provided balancing to atmospheric pressure. The volume of gaseous product was measured and collected in a gas bulb, which previously contains water that saturated with CO_2 . The gas volume was measured in $\pm 10\%$ precision. Gas samples were taken using gas tight syringes. The mixture remaining in the reactor was washed and filtered in order to separate the solid product. 1–2 drops of concentrated sulphuric acid was added liquid product samples to reduce the pH of the solution. Solid product samples were dried overnight in oven. The inside of reactor was washed with THF (tetrahydrofuran) after removal of the products in reactor. Analysis of SCWG products were conducted by using equipments below:

- ❖ GC: Gas Chromatography with FID-TCD detectors, HP 7890A Wilmington–USA.
- ❖ TOC: Shimadzu Total Organic Carbon analyser, TOC-VCPH.
- ❖ HPLC: Shimadzu Liquid Chromatography System, LC-20A.
- ❖ Colorimeter: Jenway 6051 Colorimeter.
- ❖ TOC-SSM.

4.2.2 Analytical methods

4.2.2.1 Gas phase analysis

Gaseous product was analyzed by gas chromatography (GC). The gas chromatograph (HP 7890A, Wilmington–USA) was equipped with serially connected Hayesep Q 80/100 mesh (0.5 m long $\times$ 2 mm i.d.), Hayesep Q 80/100 mesh (1.8 m long $\times$ 2 mm i.d.), Molsieve 5A 60/80 mesh (2.4 m long $\times$ 2 mm i.d.), Hayesep Q 80/100 mesh (0.9 m long $\times$ 2 mm i.d.), Molsieve 5A 60/80 mesh (2.4 m long $\times$ 2 mm i.d.), DB-1 (pre-column) and HP-Plot Al_2O_3 S (25 m long $\times$ 0.32 mm i.d.) columns. Two thermal conductivity detectors (TCD) and a flame

ionization detector (FID) were arranged serially. Helium was used as a carrier gas. The oven temperature firstly was held at 60 °C isothermal for 1 min, then reached to 80 °C at a rate of 20 °C min⁻¹, and finally reached to 120 °C at a rate of 30 °C min⁻¹ for 2.66 min.

Gas sample was injected by gas tight syringe (Figure 4.2.2.1.1). GC was calibrated with standard gas mixture supplied by HatGaz Company in Kocaeli, Turkey. The composition of the gaseous products (H₂, CO₂, CO and C₁–C₄ hydrocarbons) was measured by gas chromatographic methods. The standard deviation for the results of gas composition was found to be ± 2 %.

Some technical features and operating condition of gas chromatography and its picture are given in Table 4.2.2.1.1 and Figure 4.2.2.1.2, respectively.



Figure 4.2.2.1.1 Gas tight syringe.

Table 4.2.2.1.1 Technical features and operating conditions of gas chromatography.

GC Model	HP7890A
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)
Temperature Program	60°C / min, 20°C/ min speed to 80°C 30°C/ min speed to 120°C 2.66 min.
Carrier Gas	Helium
Operating Mode	Split (Range = 80:1, Flow: 60 mL/min)
Injection Temperature	250 °C
Detector Types and Operating Temperatures	Front signal – FID- 250°C Back signal – TCD- 250°C Auxiliary signal – TCD- 250°C



Figure 4.2.2.1.2 Picture of gas chromatography.

4.2.2.2 Liquid phase analysis

Total Organic Carbon Analyzer (TOC)

Amounts of total carbon (TC) and inorganic carbon (IC) in liquid products are analyzed by TOC analyzer (Figure 4.2.2.2.1).



Figure 4.2.2.2.1 Picture of TOC analyzer.

High Pressure Liquid Chromatography (HPLC)

The amounts of carboxylic acids, aldehydes, ketones and furfurals occur in the aqueous solutions were analyzed using High Performance Liquid Chromatography (HPLC). HPLC analyses were executed using a Shimadzu LC-20A series liquid chromatography device (Figure 4.2.2.2.2). The HPLC system comprised a DGU-20AS degassing module, LC-20AT gradient pump, CTO-10ASVP chromatography oven and SPD-20 multi-wavelength ultraviolet detector.

Chromatographic separation was achieved using a 250mm×4.6mm Intersil ODS-3 column (GL Science, Japan). This is a C18 reversed-phase column. A Cartridge Guard Column E (GL Science, Japan) was employed to protect the analytical column. Calibration curves were constructed by plotting a linear regression of the average response factor (n=5) versus the analyte concentration for all calibration standards analyzed.

For the analysis of carboxylic acids, phenols and furfurals Method 1 (Table 4.2.2.2.1) was applied. But, analysis of aldehydes cannot be performed directly. Derivatization of these compounds are obligatory to analyse with HPLC. HPLC analysis of formaldehyde, acetaldehyde, hydroxyacetone, propionaldehyde, acetone, butyraldehyde and isobutyraldehyde standards were performed by derivatization with 2,4-dinitrophenylhydrazine. Method 2 (Table 4.2.2.2.1) was used for this analysis. The derivatization reaction is:

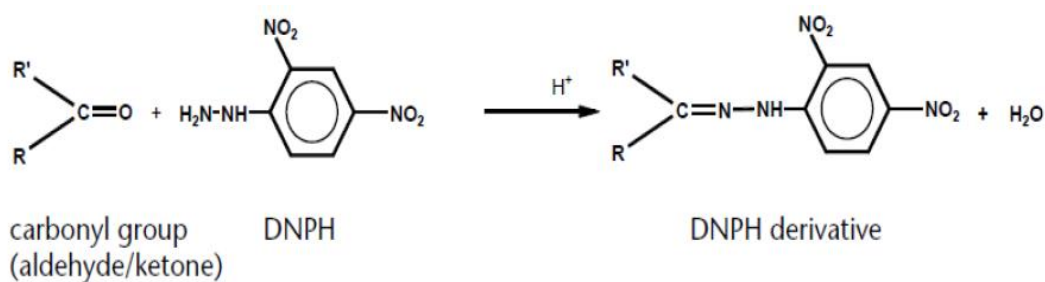


Table 4.2.2.2.1 Operating conditions of HPLC for Method 1 and 2.

	Method I	Method II
Column	Inertsil ODS-3 (250 mm length x 4.6 I.D.)	Inertsil ODS-3 (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 (80/20: vol/vol.)	A: Water B: Methanol
Flowrate	1 mL/min	1 mL/min
Detector	UV	UV
Wavelength	Variable with time	365 nm
Column temperature	30°C	30°C
Detector temperature	30°C	30°C
Injection volume	20 µL	20 µL
Low temperature gradient program of mobil phase	0. min. 90 % A ve 10% B 0. min. detector wavelength 210 nm 5. min. detector wavelength 290 nm 7. min. detector wavelength 285 nm 11. min. detector wavelength 278 nm 15. min detector wavelength 232 nm 17. min. 90% A ve 10% B 19. min. detector wavelength 290 nm 25. min. 65% A ve 35% B 27.5. min. detector wavelength 290 nm 55. min. 65% A ve 35% B	0. 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



Figure 4.2.2.2.2 High Performance Liquid Chromatography.

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 put, consequently. The final solution was stirred at room temperature for 1 hour. After that, mixed with 2 mL of acetonitrile pursued by syringe injection of 20 μL into the HPLC apparatus.

The standard aldehydes were of analytical grade (Merck, Aldrich). On the other hand, methanol and acetonitrile were of HPLC grade (Merck). Water was purified using a ultra-pure water device. 2,4- Dinitrophenylhydrazine (BDH) was purified by three successive recrystallizations from methanol. The aldehyde-DNPHs were gained: 2,4-dinitrophenylhydrazine (0.4 g; ca. 2 mmol) was dissolved in concentrated sulfuric acid (2 mL) and distilled water (3 mL). The standard aldehydes (0.1 g), dissolved in ethanol (15 mL), were put into this solution. The suitable aldehyde-DNPHs were separated by filtration and purified (twice) by recrystallization from absolute ethanol.

4.2.2.3 Solid phase analysis

Total Organic Carbon Analyzer (TOC) – Solid Sample Measurement (SSM)

After gasification, solid residues were recovered via filtration of the reaction by-product as stated in experimental procedure part. The solids are then dried in an oven which is set at 100°C all night long. Combining the SSM with a TOC analyzer allows analysis of many solid samples in addition aqueous samples, consisting soil, sludge, and sediments. TOC-SSM analyzer is seen in Figure 4.2.2.2.1.

5. EVALUATION OF RESULTS

In this experimental study, the effect of temperature, pressure and catalyst on evolution of gaseous, liquid and solid products in supercritical water gasification of Peapod and red kidney bean shells as wastes was investigated. Presence and absence of catalyst temperature experiments will be done according to design of experimental plans at 300, 400, 500, 600°C. Trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$), Dolomite ($\text{CaMg}(\text{CO}_3)_2$), Borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), Potassium Hydroxide (KOH) and Sodium Hydroxide (NaOH) were used as catalyst. As a consequence of reaction in the absence of catalyst and in the presence of 10 wt. % Trona, Dolomite, Borax, Potassium Hydroxide and Sodium Hydroxide catalyst generated some products and expected changes were observed with solid, liquid and gas analysis devices (GC, GC-MS, HPLC, TOC, TOC-SSM). The experimental results are shown in Table 5.1 to 5.12.

Table 5.1 Experimental results of SCWG of Peas Wastes without catalyst at different temperatures (300, 400, 500, 600 °C).

Experiment Temperature, [°C]	300	400	500	600
Reaction Pressure, [atm]	92	217	365	440
Catalyst Type, [10 wt %]	No Catalyst	No Catalyst	No Catalyst	No Catalyst
Gas Product Composition, [mol%]				
CH₄	0.4	6.3	18.9	23.2
H₂	2.6	19.2	28.9	31.2
CO₂	91.6	70.4	46.1	39.9
CO	5.1	0.6	0.3	0.2
C₂-C₄	0.3	3.5	5.8	5.4
Gas Product, [mol/kg Biomass]				
CH₄	0.04	1.2	5.6	7.7
H₂	0.3	3.8	8.4	10.4
CO₂	9.5	13.9	13.4	13.2
CO	0.5	0.1	0.08	0.07
C₂-C₄	0.03	0.7	1.7	1.8
Total Gas Product, [g/kg Biomass]	434.4	669.2	766.2	798.8
Gas Yield, [%]	28.9	48.1	63.4	69.4
Liquid Yield, [%]	37.9	25.2	15.4	12.6
Solid Yield, [%]	31.3	23.0	19.5	17.3
TOC, [mg/L]	1730	1150	610	480
Solid Product, [g/kg Biomass]	212.9	162.0	121.2	111.1

Table 5.2 Experimental results of SCWG of Peas Wastes with Trona at different temperatures (300, 400, 500, 600 °C).

Experiment Temperature, [°C]	300	400	500	600
Reaction Pressure, [atm]	90	243	307	460
Catalyst Type, [10 wt %]	Trona	Trona	Trona	Trona
Gas Product Composition, [mol%]				
CH₄	0.8	6.5	19.6	24.1
H₂	4.8	23.2	29.6	34.5
CO₂	85.3	66.1	43.9	36.2
CO	8.5	0.5	0.3	0.1
C₂-C₄	0.6	3.6	6.8	5.1
Gas Product, [mol/kg Biomass]				
CH₄	0.1	1.6	6.4	9.6
H₂	0.6	5.5	9.7	13.8
CO₂	11.2	15.7	14.4	14.5
CO	1.1	0.1	0.1	0.03
C₂-C₄	0.08	0.9	2.3	2.0
Total Gas Product, [g/kg Biomass]	529.6	766.2	850.2	900
Gas Yield, [%]	35.8	55.9	75.3	83.2
Liquid Yield, [%]	39.0	24.4	13.7	9.5
Solid Yield, [%]	23.6	15.0	10.0	6.3
TOC, [mg/L]	1780	1120	627	435
Solid Product, [g/kg Biomass]	199.6	111.1	87.9	55.5

Table 5.3 Experimental results of SCWG of Peas Wastes with Dolomite at different temperatures (300, 400, 500, 600 °C).

Experiment Temperature, [°C]	300	400	500	600
Reaction Pressure, [atm]	95	332	348	450
Catalyst Type, [10 wt %]	Dolomite	Dolomite	Dolomite	Dolomite
Gas Product Composition, [mol%]				
CH₄	0.8	6.9	19.3	22.8
H₂	3.8	22.1	29.1	34.5
CO₂	87.8	66.1	44.6	37.8
CO	7.4	0.8	0.4	0.1
C₂-C₄	0.2	4.1	6.6	4.8
Gas Product, [mol/kg Biomass]				
CH₄	0.1	1.6	6.1	8.8
H₂	0.5	5.1	9.2	13.2
CO₂	11.3	15.3	14.0	14.5
CO	1.0	0.2	0.13	0.04
C₂-C₄	0.02	0.9	2.1	1.8
Total Gas Product, [g/kg Biomass]	528.6	750.6	819.6	878.3
Gas Yield, [%]	35.4	55.2	72.4	79.3
Liquid Yield, [%]	34.6	25.0	12.7	9.6
Solid Yield, [%]	26.2	15.5	14.1	9.1
TOC, [mg/L]	1580	1140	580	440
Solid Product, [g/kg Biomass]	240.7	152.7	138.8	101.8

Table 5.4 Experimental results of SCWG of Peas Wastes with Borax at different temperatures (300, 400, 500, 600 °C).

Experiment Temperature, [°C]	300	400	500	600
Reaction Pressure, [atm]	97	250	315	470
Catalyst Type, [10 wt %]	Borax	Borax	Borax	Borax
Gas Product Composition, [mol%]				
CH₄	0.7	6.5	19.1	21.5
H₂	4.2	20.7	28.5	33.8
CO₂	87.0	68.2	45.6	39.8
CO	7.6	0.7	0.4	0.2
C₂-C₄	0.5	3.9	6.4	4.7
Gas Product, [mol/kg Biomass]				
CH₄	0.1	1.6	6.0	8.4
H₂	0.5	5.0	9.0	13.2
CO₂	10.9	16.3	14.4	15.5
CO	0.95	0.16	0.12	0.08
C₂-C₄	0.06	0.9	2.0	1.8
Total Gas Product, [g/kg Biomass]	511.2	793.3	831.0	917.0
Gas Yield, [%]	34.4	57.9	72.9	81.1
Liquid Yield, [%]	39.5	22.1	12.6	10.1
Solid Yield, [%]	23.8	16.4	14.3	7.3
TOC, [mg/L]	1800	1010	575	460
Solid Product, [g/kg Biomass]	175.9	115.7	100.9	64.8

Table 5.5 Experimental results of SCWG of Peas Wastes with KOH at different temperatures (300, 400, 500, 600 °C).

Experiment Temperature, [°C]	300	400	500	600
Reaction Pressure, [atm]	92	280	380	475
Catalyst Type, [10 wt %]	KOH	KOH	KOH	KOH
Gas Product Composition, [mol%]				
CH₄	0.4	8.5	19.5	24.5
H₂	3.4	29.9	30.6	31.9
CO₂	84.5	57.2	43.8	38.2
CO	11.4	0.6	0.2	0.1
C₂-C₄	0.3	3.8	5.9	5.3
Gas Product, [mol/kg Biomass]				
CH₄	0.05	2.3	6.5	9.6
H₂	0.4	8.2	10.1	12.6
CO₂	10.4	15.7	14.5	12.3
CO	1.4	0.16	0.07	0.03
C₂-C₄	0.04	1.1	2.0	2.1
Total Gas Product, [g/kg Biomass]	500.0	792.5	844.2	804.8
Gas Yield, [%]	34.0	58.9	73.7	83.3
Liquid Yield, [%]	38.7	24.2	13.2	6.5
Solid Yield, [%]	25.0	15.2	10.0	7.9
TOC, [mg/L]	1765	1108	605	295
Solid Product, [g/kg Biomass]	175.9	138.8	92.6	74.0

Table 5.6 Experimental results of SCWG of Peas Wastes with NaOH at different temperatures (300, 400, 500, 600 °C).

Experiment Temperature, [°C]	300	400	500	600
Reaction Pressure, [atm]	112	235	390	470
Catalyst Type, [10 wt %]	NaOH	NaOH	NaOH	NaOH
Gas Product Composition, [mol%]				
CH₄	0.4	6.6	19.6	25.2
H₂	5.3	25.7	29.9	30.5
CO₂	84.8	62.7	43.6	38.3
CO	8.6	2.2	0.5	0.2
C₂-C₄	0.9	2.8	6.4	5.8
Gas Product, [mol/kg Biomass]				
CH₄	0.05	1.7	6.8	9.1
H₂	0.6	6.4	10.4	11.0
CO₂	10.0	15.8	15.2	13.0
CO	1.0	0.6	0.12	0.08
C₂-C₄	0.1	0.7	2.2	2.1
Total Gas Product, [g/kg Biomass]	474.0	780.0	889.8	825.8
Gas Yield, [%]	33.3	56.4	71.9	79.8
Liquid Yield, [%]	40.0	26.5	12.1	7.1
Solid Yield, [%]	26.3	14.2	13.1	9.4
TOC, [mg/L]	1825	1210	550	315
Solid Product, [g/kg Biomass]	185.2	120.3	111.1	88.3

Table 5.7 Experimental results of SCWG of Red Kidney Beans Wastes without catalyst at different temperatures (300, 400, 500, 600 °C).

Experiment Temperature, [°C]	300	400	500	600
Reaction Pressure, [atm]	108	220	380	490
Catalyst Type, [10 wt %]	No Catalyst	No Catalyst	No Catalyst	No Catalyst
Gas Product Composition, [mol%]				
CH₄	0.3	6.6	18.2	24.1
H₂	3.1	18.1	30.8	34.5
CO₂	86.9	70.9	44.3	38.0
CO	9.4	0.7	0.4	0.2
C₂-C₄	0.3	3.7	6.3	3.2
Gas Product, [mol/kg Biomass]				
CH₄	0.04	1.3	5.3	8.6
H₂	0.3	3.6	8.9	12.2
CO₂	9.5	10.0	12.9	13.5
CO	1.0	0.13	0.1	0.08
C₂-C₄	0.03	0.8	1.8	1.1
Total Gas Product, [g/kg Biomass]	445.2	720.8	814.3	837.4
Gas Yield, [%]	31.1	50.3	66.6	72.8
Liquid Yield, [%]	39.0	26.1	15.5	12.4
Solid Yield, [%]	26.0	21.7	16.8	12.6
TOC, [mg/L]	1780	1190	705	565
Solid Product, [g/kg Biomass]	166.9	139.8	108.3	90.2

Table 5.8 Experimental results of SCWG of Red Kidney Beans Wastes with Trona at different temperatures (300, 400, 500, 600 °C).

Experiment Temperature, [°C]	300	400	500	600
Reaction Pressure, [atm]	110	259	370	470
Catalyst Type, [10 wt %]	Trona	Trona	Trona	Trona
Gas Product Composition, [mol%]				
CH₄	0.4	6.8	20.0	24.7
H₂	4.1	25.4	31.1	35.7
CO₂	85.3	63.6	41.3	34.2
CO	9.6	0.8	0.4	0.1
C₂-C₄	0.6	3.4	7.2	5.3
Gas Product, [mol/kg Biomass]				
CH₄	0.06	1.7	6.5	10.2
H₂	0.6	6.3	10.2	14.6
CO₂	12.0	15.6	13.6	14.0
CO	1.4	0.3	0.14	0.03
C₂-C₄	0.08	0.8	2.4	2.2
Total Gas Product, [g/kg Biomass]	522.6	780.1	835.8	903.5
Gas Yield, [%]	39.8	57.6	76.5	84.7
Liquid Yield, [%]	39.4	30.7	12.9	8.1
Solid Yield, [%]	18.4	11.5	8.7	4.7
TOC, [mg/L]	1800	1400	590	370
Solid Product, [g/kg Biomass]	126.3	85.7	72.2	51.4

Table 5.9 Experimental results of SCWG of Red Kidney Beans Wastes with Dolomite at different temperatures (300, 400, 500, 600 °C).

Experiment Temperature, [°C]	300	400	500	600
Reaction Pressure, [atm]	112	250	370	480
Catalyst Type, [10 wt %]	Dolomite	Dolomite	Dolomite	Dolomite
Gas Product Composition, [mol%]				
CH₄	0.7	5.9	19.7	23.7
H₂	3.9	17.6	29.6	35.5
CO₂	84.7	72.3	43.0	35.6
CO	10.4	1.1	0.6	0.2
C₂-C₄	0.3	3.1	6.9	5.0
Gas Product, [mol/kg Biomass]				
CH₄	0.08	1.4	6.3	9.1
H₂	0.5	3.9	9.5	13.6
CO₂	10.8	16.0	13.8	13.7
CO	1.3	0.23	0.2	0.07
C₂-C₄	0.04	0.7	2.2	1.9
Total Gas Product, [g/kg Biomass]	515.5	768.6	921.4	861.2
Gas Yield, [%]	35.7	55.8	75.3	80.2
Liquid Yield, [%]	35.1	24.2	9.9	7.9
Solid Yield, [%]	26.8	16.1	12.3	9.2
TOC, [mg/L]	1600	1105	455	360
Solid Product, [g/kg Biomass]	221.1	153.4	111.9	108.3

Table 5.10 Experimental results of SCWG of Red Kidney Beans Wastes with Borax at different temperatures (300, 400, 500, 600 °C).

Experiment Temperature, [°C]	300	400	500	600
Reaction Pressure, [atm]	112	255	365	470
Catalyst Type, [10 wt %]	Borax	Borax	Borax	Borax
Gas Product Composition, [mol%]				
CH₄	0.6	5.6	20.5	23.7
H₂	8.9	22.6	30.5	34.2
CO₂	86.6	67.3	41.5	36.8
CO	8.5	0.9	0.3	0.1
C₂-C₄	0.4	3.6	7.2	5.2
Gas Product, [mol/kg Biomass]				
CH₄	0.09	1.3	6.6	9.0
H₂	0.5	5.6	9.9	13.0
CO₂	12.0	16.7	13.4	14.0
CO	1.2	0.2	0.09	0.03
C₂-C₄	0.06	0.9	2.3	2.0
Total Gas Product, [g/kg Biomass]	566.4	808.4	809.5	866.8
Gas Yield, [%]	36.2	59.8	75.7	81.7
Liquid Yield, [%]	37.7	21.5	10.5	9.1
Solid Yield, [%]	25.8	15.6	12.1	8.0
TOC, [mg/L]	1720	980	480	415
Solid Product, [g/kg Biomass]	144.4	108.3	99.2	55.0

Table 5.11 Experimental results of SCWG of Red Kidney Beans Wastes with KOH at different temperatures (300, 400, 500, 600 °C).

Experiment Temperature, [°C]	300	400	500	600
Reaction Pressure, [atm]	100	260	375	470
Catalyst Type, [10 wt %]	KOH	KOH	KOH	KOH
Gas Product Composition, [mol%]				
CH₄	0.2	6.4	20.5	25.7
H₂	3.8	34.2	35.7	35.2
CO₂	86.0	55.3	37.3	33.2
CO	9.7	0.6	0.3	0.1
C₂-C₄	0.3	3.5	6.2	5.8
Gas Product, [mol/kg Biomass]				
CH₄	0.03	1.8	7.1	10.2
H₂	0.5	9.5	12.4	15.3
CO₂	11.2	15.3	13.0	13.2
CO	1.3	0.17	0.1	0.04
C₂-C₄	0.04	1.0	2.1	2.2
Total Gas Product, [g/kg Biomass]	532.1	765.8	737.2	863.7
Gas Yield, [%]	36.5	57.6	74.5	85.0
Liquid Yield, [%]	37.7	25.2	13.4	8.2
Solid Yield, [%]	34.1	14.3	10.4	5.4
TOC, [mg/L]	1720	1150	610	375
Solid Product, [g/kg Biomass]	180.5	115.5	85.7	54.1

Table 5.12 Experimental results of SCWG of Red Kidney Beans Wastes with NaOH at different temperatures (300, 400, 500, 600 °C).

Experiment Temperature, [°C]	300	400	500	600
Reaction Pressure, [atm]	90	260	375	470
Catalyst Type, [10 wt %]	NaOH	NaOH	NaOH	NaOH
Gas Product Composition, [mol%]				
CH₄	0.3	10.3	18.9	25.7
H₂	5.2	32.9	33.5	31.6
CO₂	82.1	50.3	40.1	36.2
CO	11.7	1.7	0.4	0.1
C₂-C₄	0.7	4.8	7.1	6.4
Gas Product, [mol/kg Biomass]				
CH₄	0.03	2.7	6.1	9.1
H₂	0.6	8.7	10.7	11.3
CO₂	9.9	13.3	12.9	13.6
CO	1.4	0.4	0.12	0.03
C₂-C₄	0.08	1.2	2.2	2.3
Total Gas Product, [g/kg Biomass]	479.7	705.0	778.0	859.4
Gas Yield, [%]	34.0	57.5	72.3	83.3
Liquid Yield, [%]	42.7	25.4	12.4	9.2
Solid Yield, [%]	20.8	14.6	12.6	4.5
TOC, [mg/L]	1950	1160	565	420
Solid Product, [g/kg Biomass]	171.5	117.3	103.7	45.1

5.1 Gas Product Results

5.1.1 Peapod results

Hydrogen, methane, carbon dioxide were identified as major product in the gas composition. Also, gas product included small amount of carbon monoxide, methane and C₂-C₄ hydrocarbons (ethane, ethylene, propane, butane). Mol % of gas compositions and gas yield as mol of gas over kg biomass from peapod were given in Tables 5.1 to 5.6 and also in Figures 5.1.1.1 to 5.1.1.12.

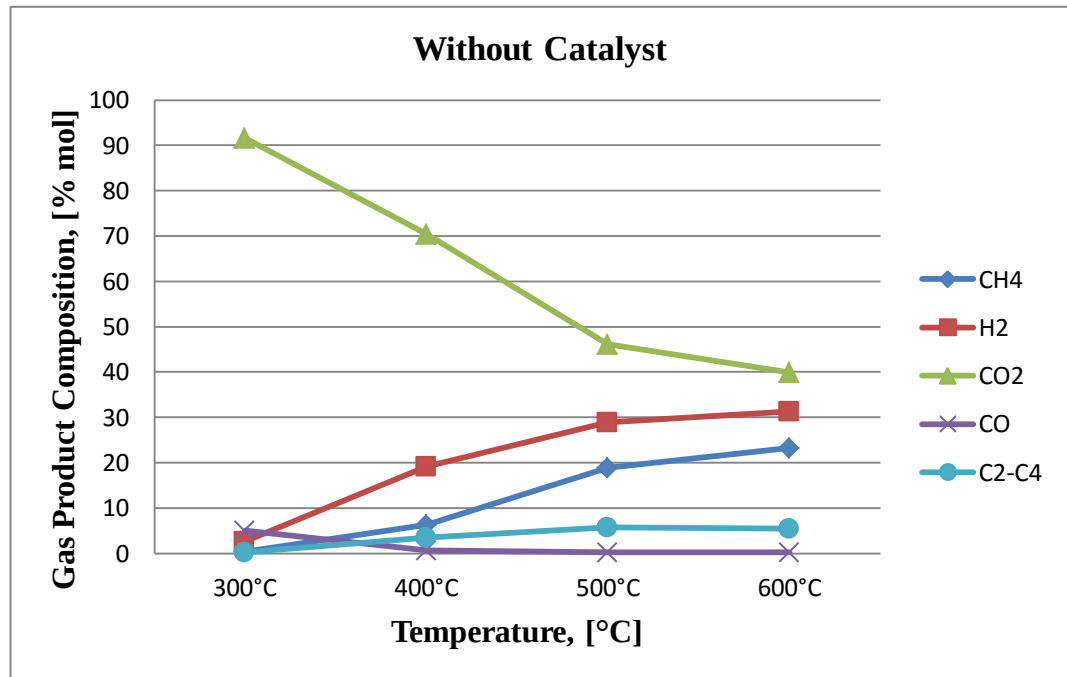


Figure 5.1.1.1 Gas composition of Peapod without catalyst at different temperatures of sub- and supercritical water.

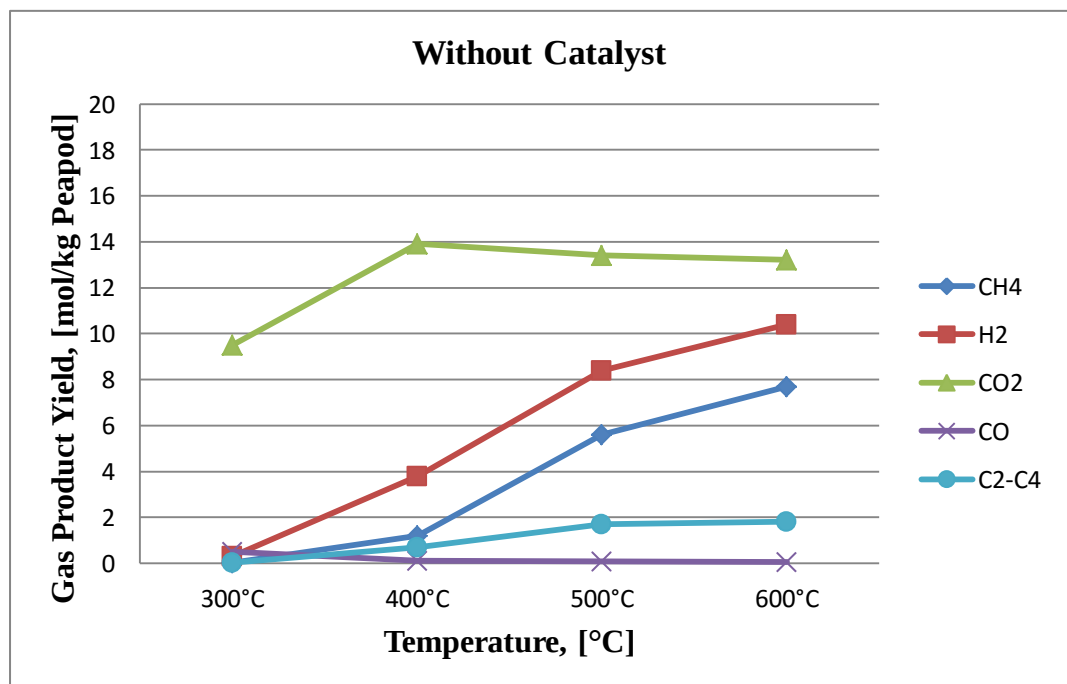


Figure 5.1.1.2 Gas product yield of Peapod without catalyst at different temperatures of sub- and supercritical water.

The gas yield should be increase with increasing temperature based on the previous studies. Unsurprisingly, the gas product yields of peapod increased with increasing temperature as shown in Table 5.1 and Figures 5.1.1.1 and 5.1.1.2. The gas yields without catalyst at 300°C, 400°C, 500°C and 600°C were found as 28.9, 48.4, 63.4 and 69.4 wt. % respectively (See Table 5.1). With increasing temperature from 300 to 600°C, mol % of H₂ increased sharply from 2.6 to 31.2, mol % of CH₄ raised from 0.4 to 23.2 %. Also, the mol % of CO₂ decreased continuously from 91.6 to 39.9 % with increasing temperature from 300°C to 600°C as expected and declining % mol of CO was found from 5.1 to 0.2 %. Additively, there was a C₂-C₄ % mol rising from 0.3 to 5.4 % mol while there was an decline from 5.8 to 5.4 at 500 to 600°C. Gas product yield of H₂ and CH₄ increased sharply, CO decreased slightly with increasing temperature. CO₂ yield was increasing between 300 and 400°C as 9.5 to 13.9 mol, however was decreasing from 13.9 to 13.4 mol between temperature 400 and 500°C and was increasing again slowly from 13.4 to 13.2 between temperature 500 and 600°C. Moles of C₂-C₄ increased slowly with increasing temperature, whereas it tend to decreased between 500 and 600°C .

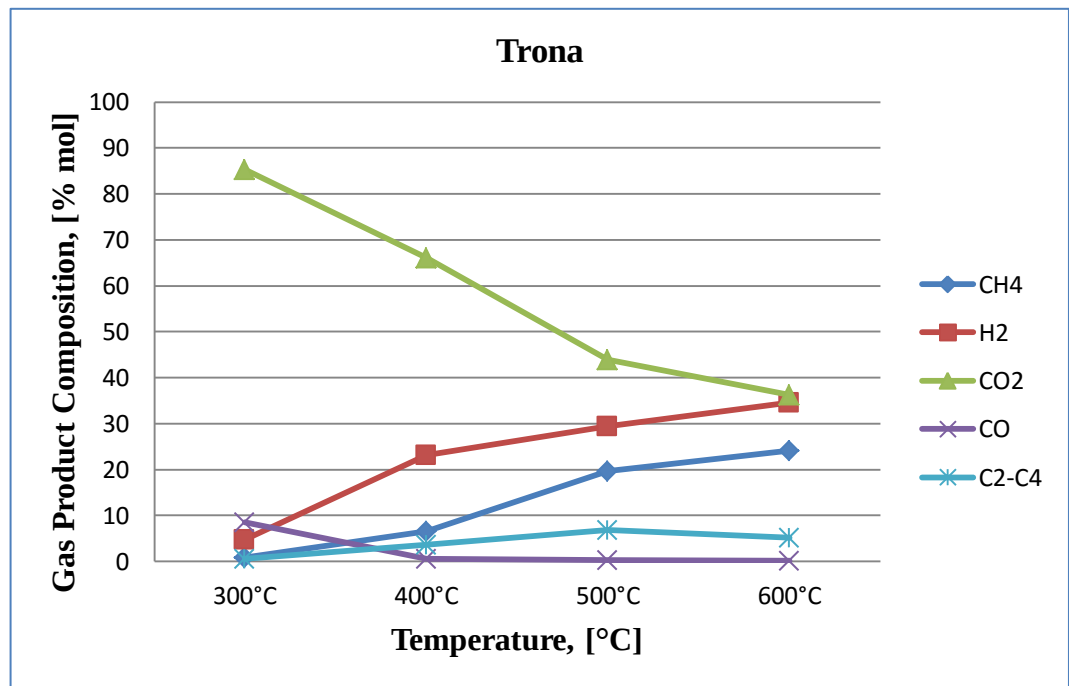


Figure 5.1.1.3 Gas composition of Peapod with Trona catalyst at different temperatures of sub- and supercritical water.

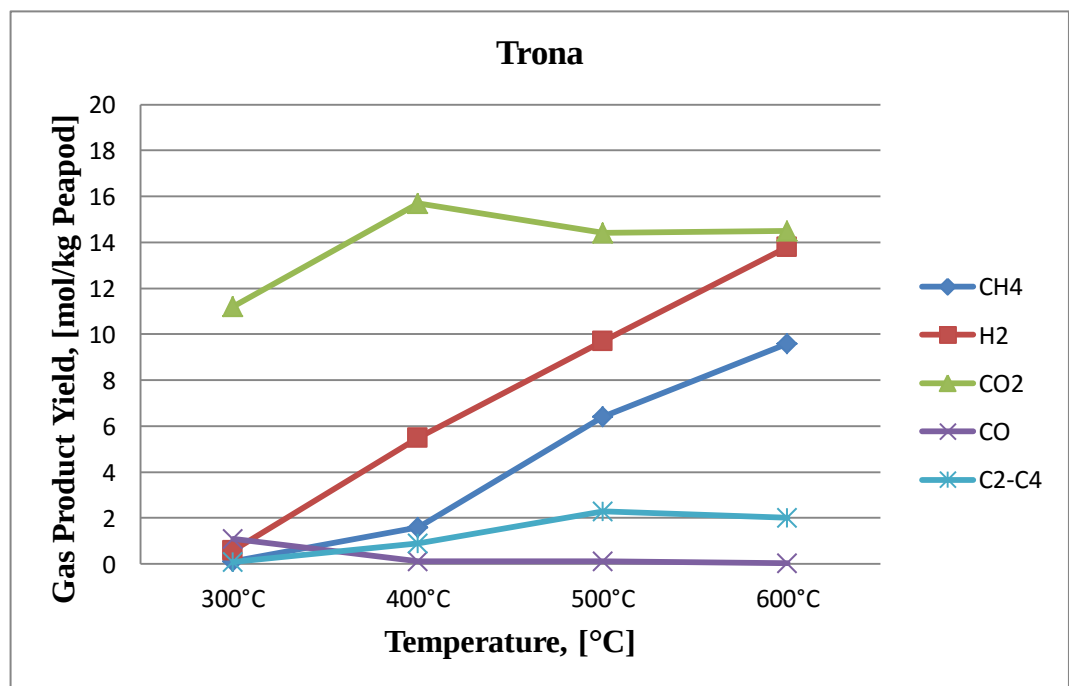


Figure 5.1.1.4 Gas product yield of Peapod with Trona catalyst at different temperatures of sub- and supercritical water.

There was a heavy increase of gas yield with Trona catalyst from 35.8 to 83.2 wt. % as seen Table 5.2 with temperature increment from 300 to 600°C. Also, 55.9 and 75.3 wt. % values of gas yield were calculated for 400 and 500°C, respectively. It can be seen, there was also rising gas yield with increasing temperature. Generally, the gas product yield increased, as temperature increased (See Figure 5.1.1.4). As it can be seen Table 5.2 and Figure 5.1.1.3, mol % of H₂ were found as 4.8, 23.2, 29.4, 34.5 mol % and mol % of CH₄ found as 0.8, 6.6, 19.6, 24.1 with rising temperature at 300, 400, 500, 600 °C, respectively. On the other hand, mol % of CO₂ decreased sharply as 85.3, 66.1, 43.9, 36.2, and mol % of CO decreased as 8.5, 0.5, 0.3, 0.1 with increasing temperature. Mol % of C₂-C₄ increased regularly between 300–500°C but decreased slightly at 600°C. Gas product yield of H₂ and CH₄ increased sharply, CO decreased slightly with increasing temperature. CO₂ yield increased between 300 and 400°C as 11.2 to 15.7 mol, however decreased from 15.7 to 14.4 mol between temperature 400 and 500°C and increased again slowly from 14.5 to 14.5 between temperature 500 and 600°C. Moles of C₂-C₄ increased slowly with increasing temperature until 500°C, although decreased at 600°C.

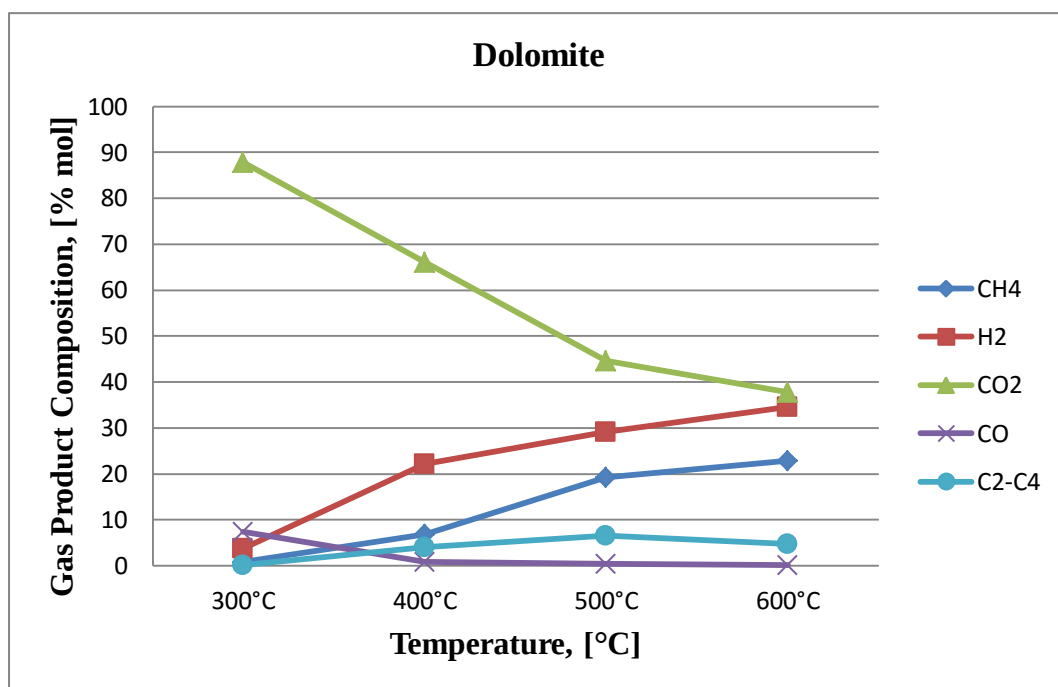


Figure 5.1.1.5 Gas composition of Peapod with Dolomite catalyst at different temperatures of sub- and supercritical water.

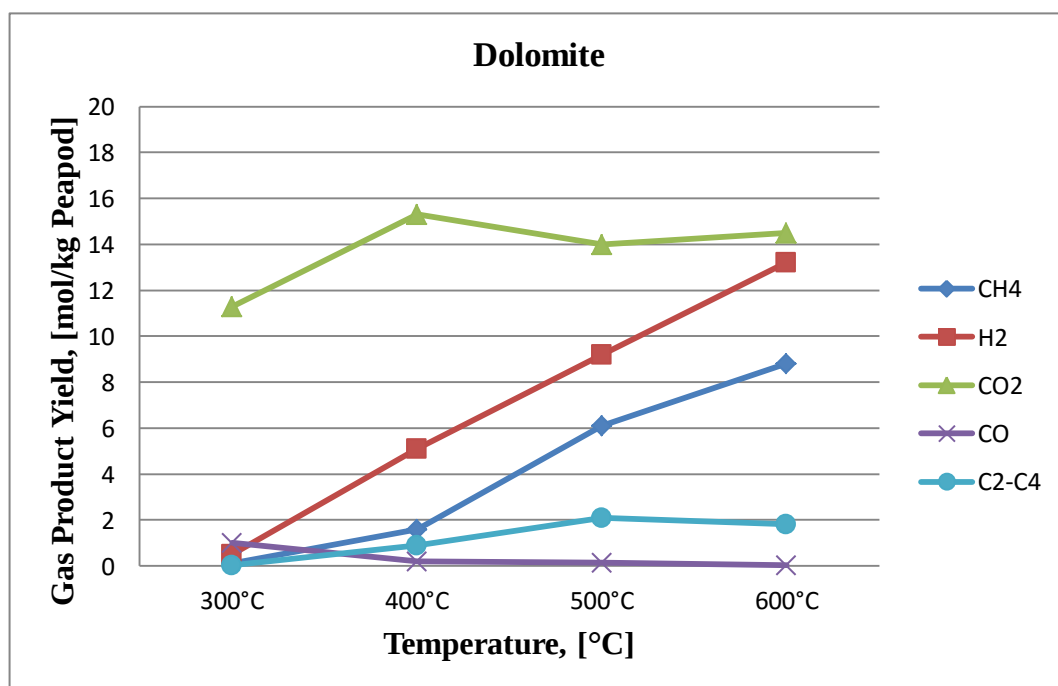


Figure 5.1.1.6 Gas product yield of Peapod with Dolomite catalyst at different temperatures of sub- and supercritical water.

The gaseous products were 35.4, 55.2, 72.4 and 79.3 wt. % for four different temperature values (See Table 5.3). Also, it can be seen gas composition and gas yield from Figure 5.1.1.4 and 5.1.1.5. Mol % of H_2 rose from 3.8 to 34.5 % at 300 to 600°C. And, mol % of CH_4 increased regularly from 0.8 to 22.8 mol %. Percentage of CO_2 and CO decreased with increasing temperature. Mol % of C_2 - C_4 were 0.2, 4.1, 6.6, and 4.8 mol % for four different temperature values. As it can be seen the values increased until 500°C and then decreased when temperature increased from 500 to 600°C. Gas product yield of H_2 and CH_4 increased sharply, CO decreased slightly with increasing temperature. CO_2 yield increased between 300 and 400°C as 11.3 to 15.3 mol, however decreased from 15.3 to 14.0 mol between temperature 400 and 500°C and increased again slowly from 14.0 to 14.5 between temperature 500 and 600°C. Moles of C_2 - C_4 increased slowly with increasing temperature, whereas it tended to decrease between 500 and 600°C .

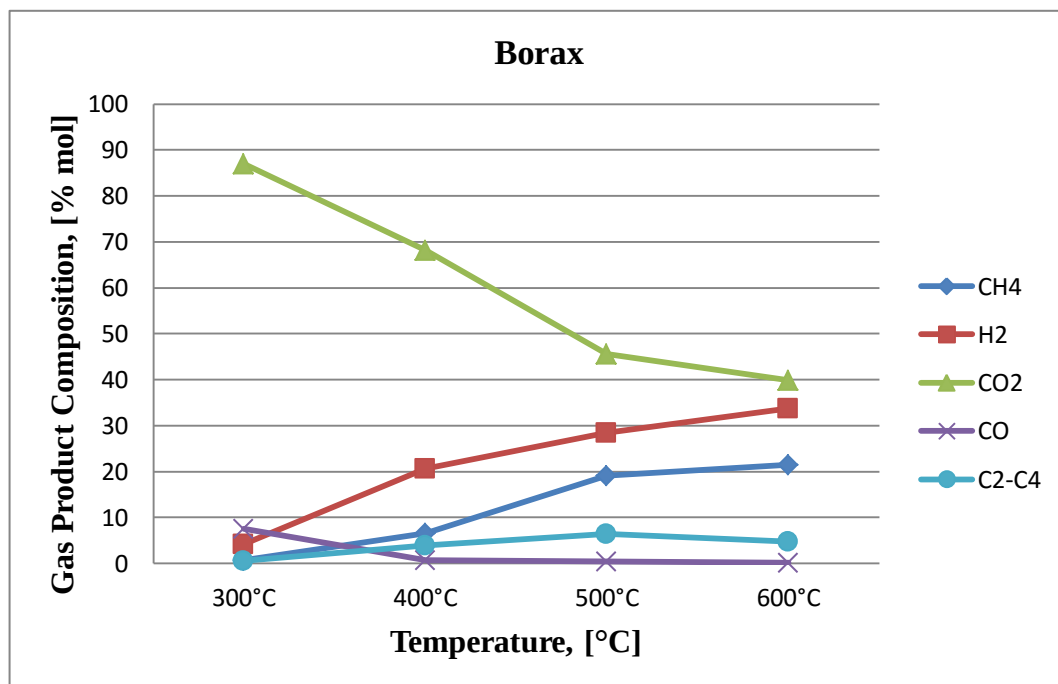


Figure 5.1.1.7 Gas composition of Peapod with Borax catalyst at different temperatures of sub- and supercritical water.

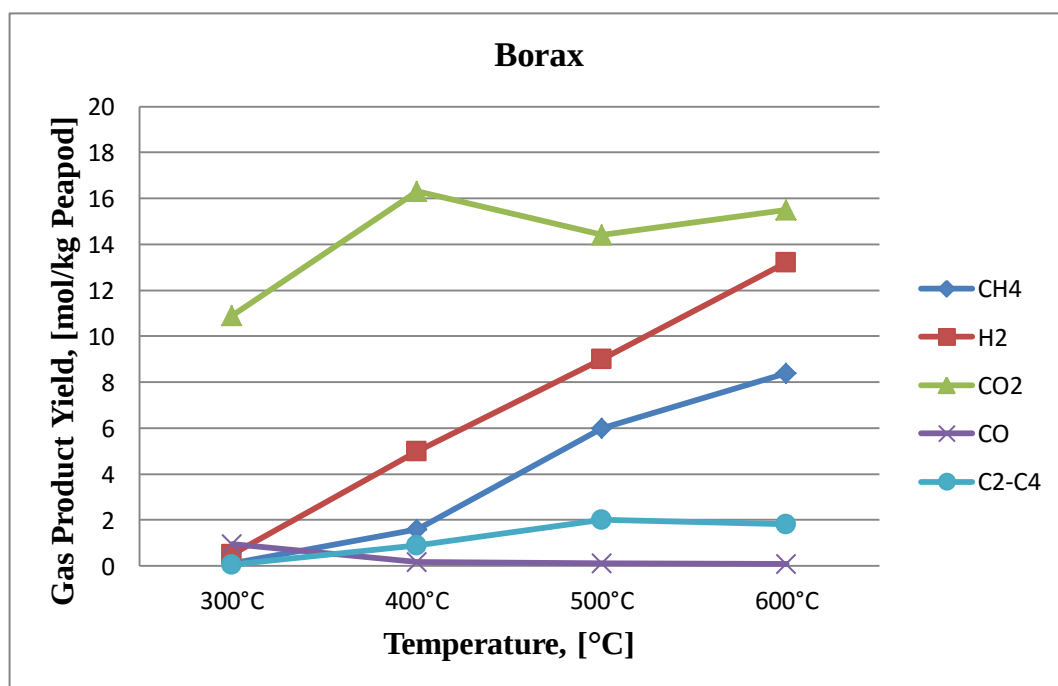


Figure 5.1.1.8 Gas product yield of Peapod with Borax catalyst at different temperatures of sub- and supercritical water.

The gas product yields of Peopod increase with increasing temperature as shown in Table 5.4 and Figures 5.1.1.7 and 5.1.1.8 for Borax Catalyst. The gas yields with Borax catalyst at 300°C, 400°C, 500°C and 600°C were found as 34.4, 57.9, 72.9 and 81.1 wt. % respectively (See Table 5.4). With increasing temperature from 300 to 600°C, mol % of H₂ increased sharply from 4.2 to 33.8, mol % of CH₄ rose from 0.7 to 21.5 %. But, the mol % of CO₂ decreased sharply from 87.0 to 39.8 % with increasing temperature from 300°C to 600°C as expected and declining % mol of CO was found from 7.6 to 0.2 %. Additively, there was a C₂-C₄ % rising from 0.5 to 4.7 % mol from 300°C to 600°C whereas there was an decline from 6.4 to 4.7 at 500 to 600°C. Gas product yield of H₂ and CH₄ increased sharply, CO decreased slowly with increasing temperature. CO₂ yield increased between 300 and 400°C as 10.9 to 16.3 mol, however decreased from 16.3 to 14.4 mol between temperature 400 and 500°C and increased again slowly from 14.4 to 15.5 between temperature 500 and 600°C. Moles of C₂-C₄ increased slowly with increasing temperature until 500°C, although decreased at 600°C.

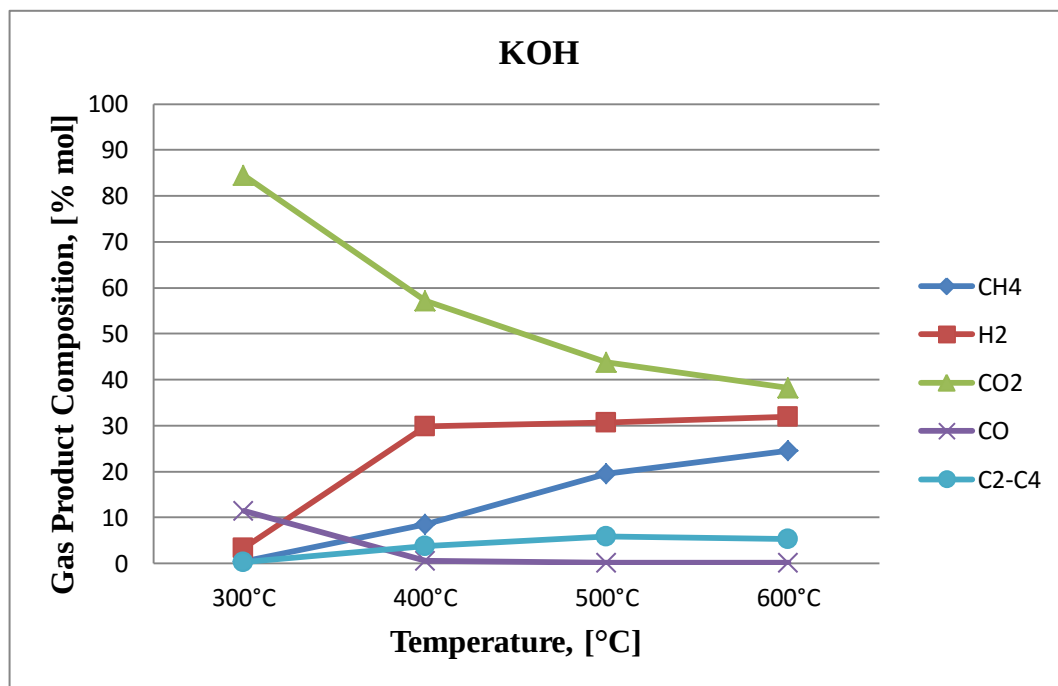


Figure 5.1.1.9 Gas composition of Peapod with KOH catalyst at different temperatures of sub- and supercritical water.

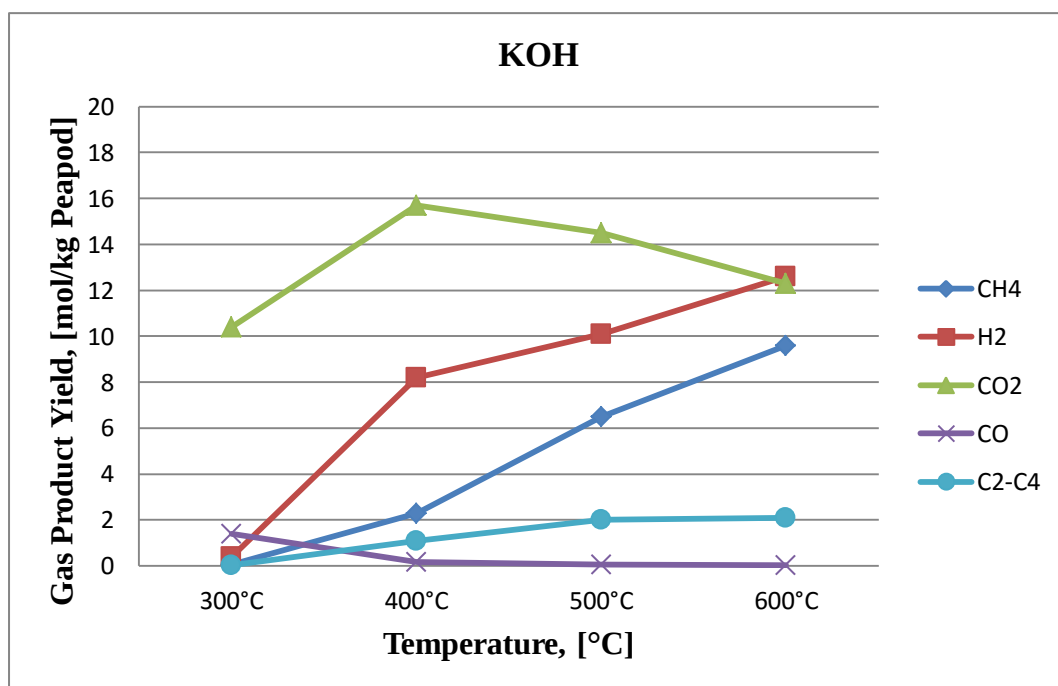


Figure 5.1.1.10 Gas product yield of Peapod with KOH catalyst at different temperatures of sub- and supercritical water.

A sharp increase of gas yield with KOH catalyst from 34.0 to 83.3 wt. % is seen in Table 5.5 with temperature increment from 300 to 600°C. Also, 58.9 and 73.7 wt. % values of gas yield were calculated for 400 and 500°C, respectively. It can be seen, gas yield rose with increasing temperature. Generally, the gas product yield increased, as temperature increased (Figure 5.1.1.10). As it can be seen Table 5.5 and Figure 5.1.1.9, mol % of H₂ were found as 3.4, 29.9, 30.6, 31.9 mol % and mol % of CH₄ found as 0.4, 8.5, 19.5, 24.5 with rising temperature at 300, 400, 500, 600 °C, respectively. Here % of H₂ is crucial. Because, it increased sharply between 300-400°C while it was close to steady above 400°C counter to mineral catalysts. On the other hand, mol % of CO₂ drop away suddenly as 84.5, 57.2, 43.8, 38.2, and mol % of CO decreased as 11.4, 0.6, 0.2, 0.1 with increasing temperature. According to the these results of CO, it dropped sharply between 300 and 400°C, before plunging down to a moderate decrease. Mol % of C₂-C₄ increased regularly between 300 – 500°C but decreased slightly at 600°C. Gas product yield of H₂ and CH₄ increased sharply, CO decreased slightly with increasing temperature. CO₂ yield increased sharply between 300 – 400°C but decreased regularly above 400°C. Moles of C₂-C₄ increased slowly with increasing temperature.

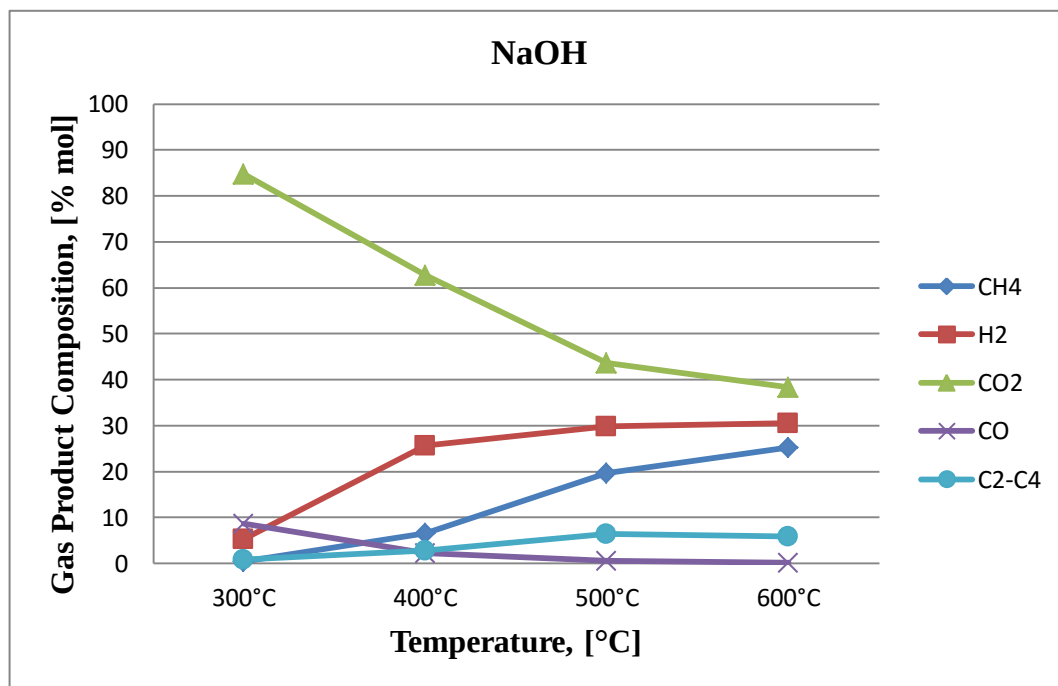


Figure 5.1.1.11 Gas composition of Peapod with NaOH catalyst at different temperatures of sub- and supercritical water.

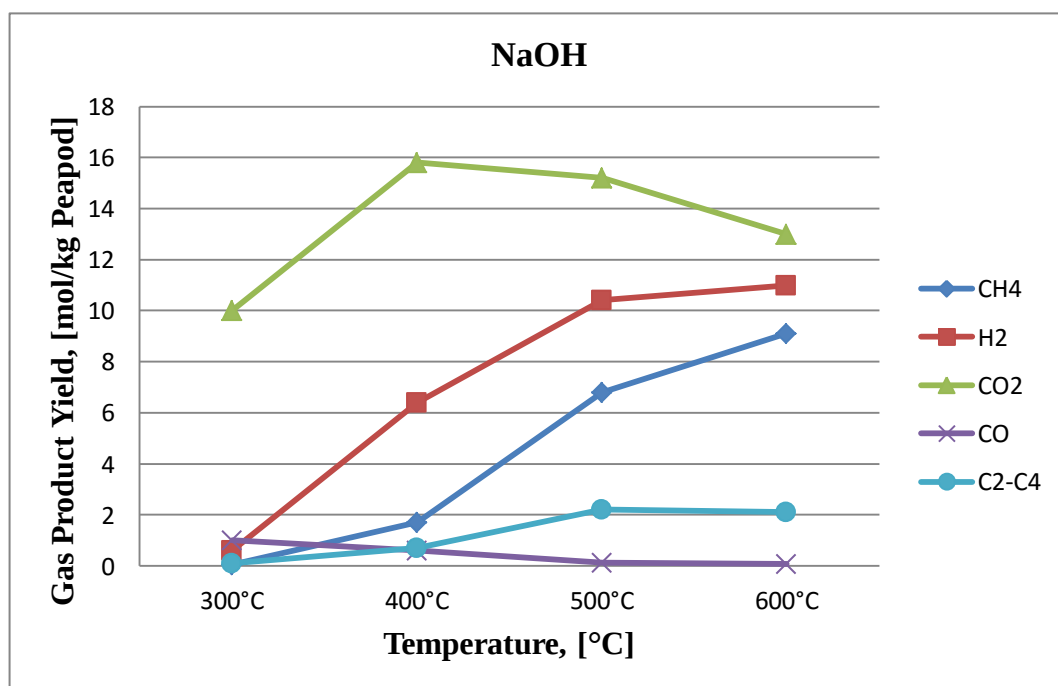


Figure 5.1.1.12 Gas product yield of Peapod with NaOH catalyst at different temperatures of sub- and supercritical water.

The gaseous products were 33.3, 56.4, 71.9 and 79.8 wt. % for four different temperature values (See Table 5.6). Figure 5.1.1.11 and 5.1.1.12 representing gas composition and gas yield. Mol % of H_2 rose from 5.3 to 30.5 % at 300 to 600°C. It increased sharply between 300-400°C while it was steady above 400°C counter to mineral catalysts like KOH. And, mol % of CH_4 increased regularly from 0.4 to 25.6 mol %. Percentage of CO_2 and CO decreased with increasing temperature. Mol % of C_2-C_4 were 0.9, 2.8, 6.4, and 5.8 mol % for four different temperature values. As it can be seen the values increased until 500°C and then decreased as temperature increased from 500 to 600°C. Gas product yield of H_2 and CH_4 increased sharply, CO yield decreased slightly with increasing temperature. CO_2 yield increased sharply between 300 and 400°C as 10.0 to 15.8 mol, however decreased moderately from 15.8 to 13.0 mol between temperature 400 and 600°C. Moles of C_2-C_4 increased slowly with increasing temperature, whereas it tended to decrease between 500 and 600°C.

5.1.2 Red kidney bean shells results

Like Peapod, Hydrogen, methane, carbon dioxide were identified as major product in the gas composition. In addition to this, there were small amount of carbon monoxide, methane and C₂-C₄ hydrocarbons (ethane, ethylene, propane, butane) in the gas product. Mol % of gas compositions and gas yield as mol of gas over kg biomass from Red Kidney Bean Shells were given in Tables 5.7 to 5.12 and also in Figures 5.1.2.1 to 5.1.2.12.

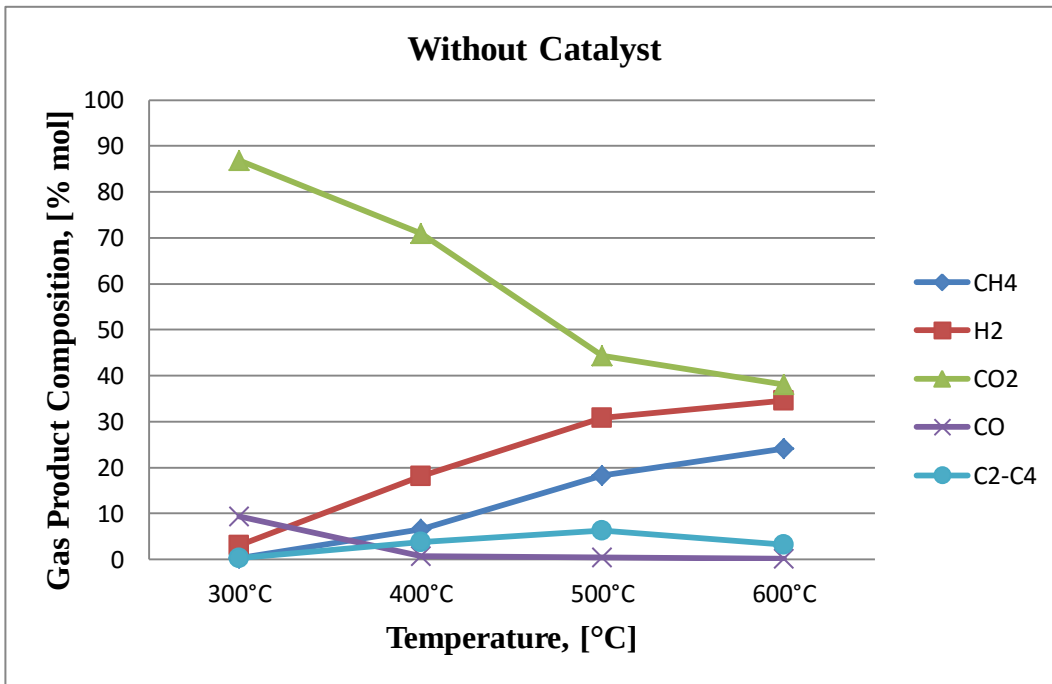


Figure 5.1.2.1 Gas composition of Red Kidney Bean Shells without catalyst at different temperatures of sub- and supercritical water.

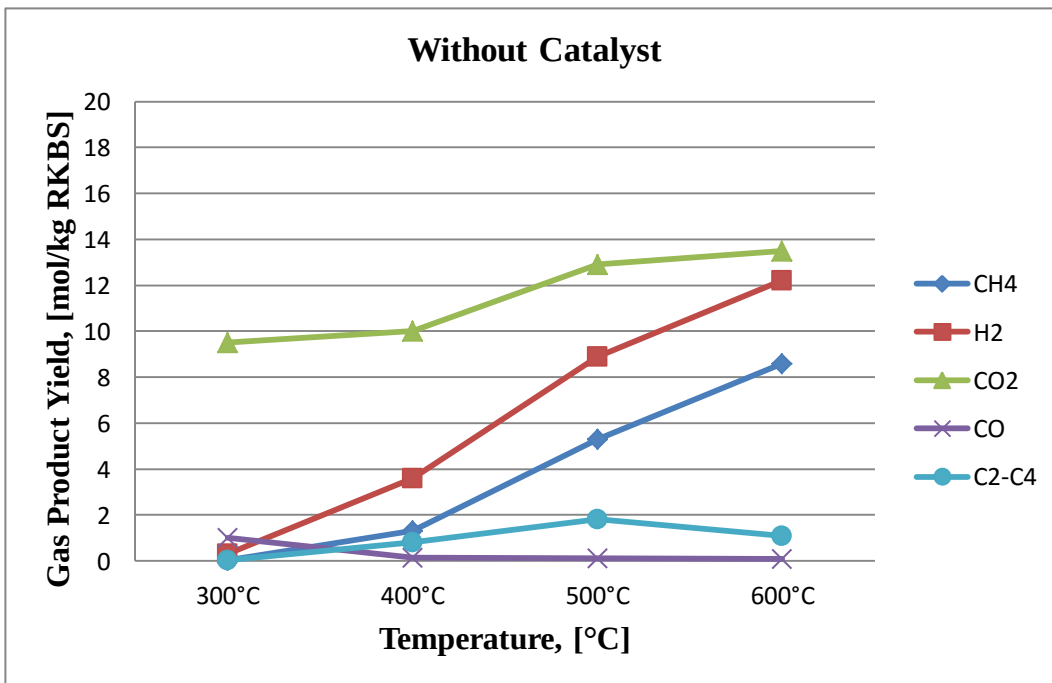


Figure 5.1.2.2 Gas product yield of Red Kidney Bean Shells without catalyst at different temperatures of sub- and supercritical water.

The gas product yields of Red Kidney Bean Shells as wastes increased with increasing temperature as shown in Table 5.7 and Figures 5.1.2.1 and 5.1.2.2. The gas yields without catalyst at 300°C, 400°C, 500°C and 600°C were calculated as 31.1, 50.3, 66.6 and 72.8 wt. % respectively (See Table 5.7). With increasing temperature from 300 to 600°C, mol % of H₂ increased sharply from 3.1 to 34.5, mol % of CH₄ rose from 0.3 to 24.1 %. Also, the mol % of CO₂ decreased continuously from 86.9 to 38.0 % with increasing temperature from 300°C to 600°C as expected and going down % mol of CO was found from 9.4 to 0.2 %. Additionally, there was a C₂-C₄ % mol rising from 0.3 to 6.3 % mol at temperature 300 to 500°C while there was a decline from 6.3 to 3.2 % mol at 500 to 600°C. Gas product yield of H₂ and CH₄ increased sharply, CO decreased slightly with increasing temperature. CO₂ yield increased between 300 and 400°C as 9.5 to 10.0 mol, however decreased from 10.0 to 12.9 mol between temperature 400 and 500°C and increased again slowly from 12.94 to 13.5 between temperature 500 and 600°C. Moles of C₂-C₄ increased slowly with increasing temperature, whereas it tended to decrease between 500 and 600°C .

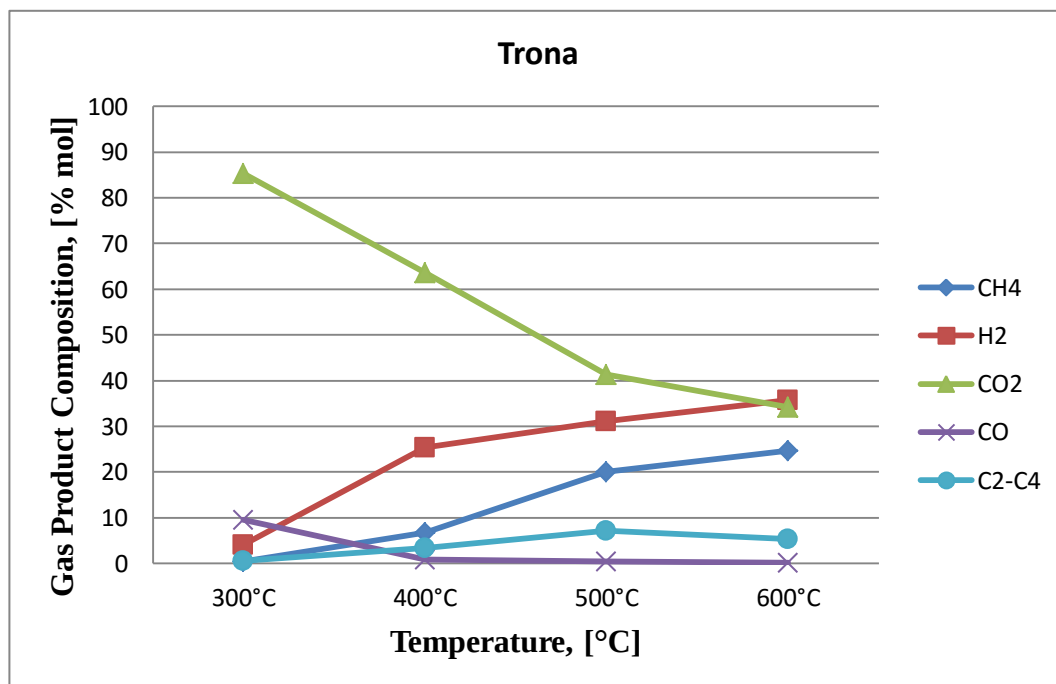


Figure 5.1.2.3 Gas composition of Red Kidney Bean Shells with Trona catalyst at different temperatures of sub- and supercritical water.

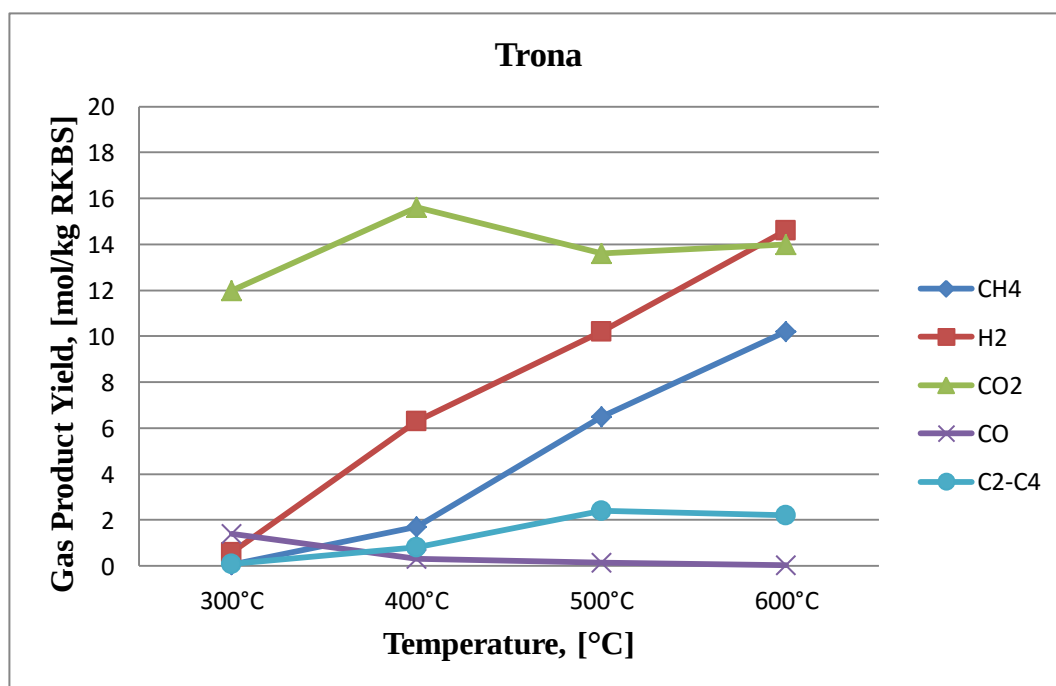


Figure 5.1.2.4 Gas product yield of Red Kidney Bean Shells with Trona catalyst at different temperatures of sub- and supercritical water.

There was a rapid increase of gas yield with Trona catalyst from 39.8 to 84.7 wt. % with increasing temperature from 300 to 600°C as represented in Table 5.8. Also, 57.6 and 76.5 wt. % values of gas yield were calculated for 400 and 500°C, respectively. It can be seen, there was also rising gas yield with increasing temperature. Generally, the gas product yield increased, as temperature increased (Figure 5.1.2.4). As it can be seen Table 5.8 and Figure 5.1.2.3, mol % of H₂ were found as 4.1, 25.4, 31.1, 35.7 and mol % of CH₄ found as 0.4, 6.8, 20.0, 24.7 with rising temperature at 300, 400, 500, 600 °C, respectively. On the other hand, mol % of CO₂ decreased sharply as 85.3, 3.6, 41.3, 34.2, and mol % of CO decreased as 9.6, 0.8, 0.4, 0.1 with increasing temperature. Mol % of C₂-C₄ increased continuously between 300 – 500°C but decreased slightly at 600°C. Gas product yield of H₂ and CH₄ increased sharply, CO decreased slightly with increasing temperature. CO₂ yield increased between 300 and 400°C as 12.0 to 15.6 mol, however decreased from 15.6 to 13.6 mol between temperature 400 and 500°C and increased again slowly from 13.6 to 14.0 between temperature 500 and 600°C. Moles of C₂-C₄ increased moderately with increasing temperature until 500°C, although decreased at 600°C.

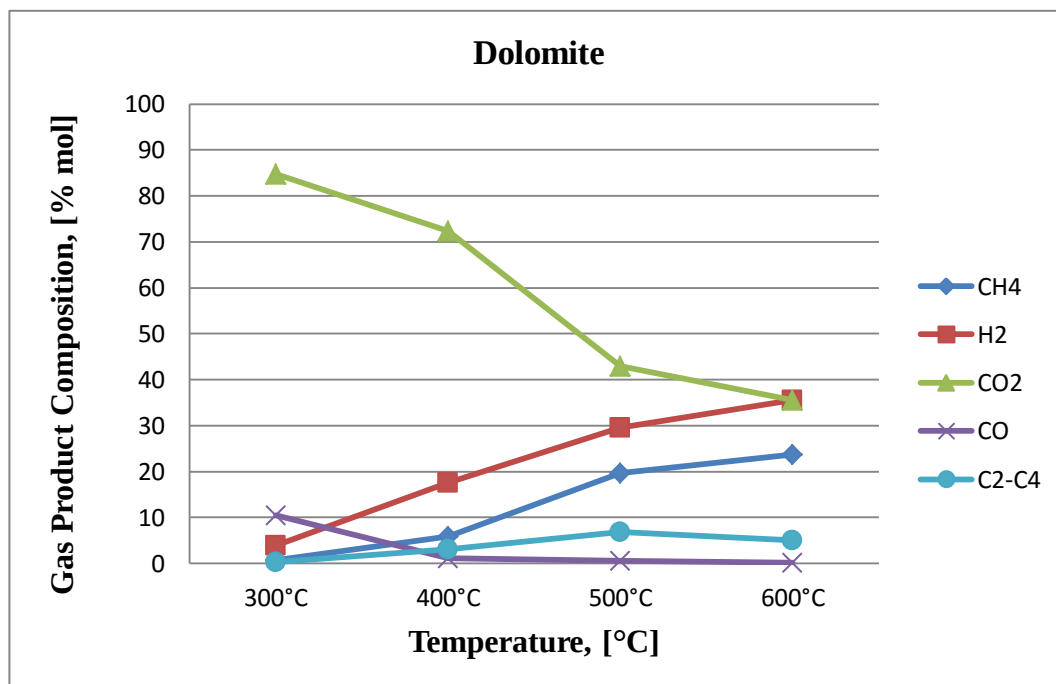


Figure 5.1.2.5 Gas composition of Red Kidney Bean Shells with Dolomite catalyst at different temperatures of sub- and supercritical water.

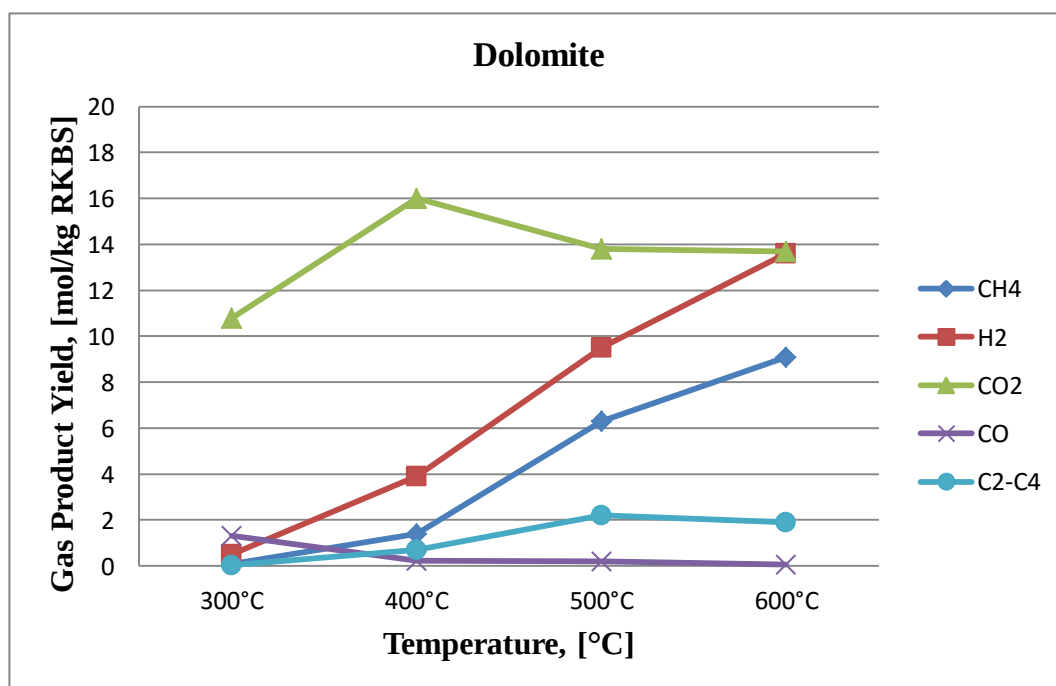


Figure 5.1.2.6 Gas product yield of Red Kidney Bean Shells with Dolomite catalyst at different temperatures of sub- and supercritical water.

The gaseous products were 35.7, 55.8, 75.3 and 80.2 wt. % for four different temperature values (See Table 5.9). Also, it can be seen gas composition and gas yield from Figure 5.1.1.5 and 5.1.1.6. Mol % of H_2 increased from 3.9 to 35.5 % at 300 to 600°C. And, mol % of CH_4 increased regularly from 0.7 to 23.7 %. Percentage of CO_2 and CO decreased with increasing temperature. Mol % of C_2 - C_4 were 0.3, 3.1, 6.9, and 5.0 mol % for four different temperature values. As it can be seen the values increased until 500°C and then decreased when temperature increased from 500 to 600°C. Gas product yield of H_2 and CH_4 increased rapidly, CO decreased gradually with increasing temperature. CO_2 yield increased sharply between 300 – 400°C but decreased moderately above 400°C. Moles of C_2 - C_4 increased slowly with increasing temperature, whereas it tended to decrease between 500 and 600°C .

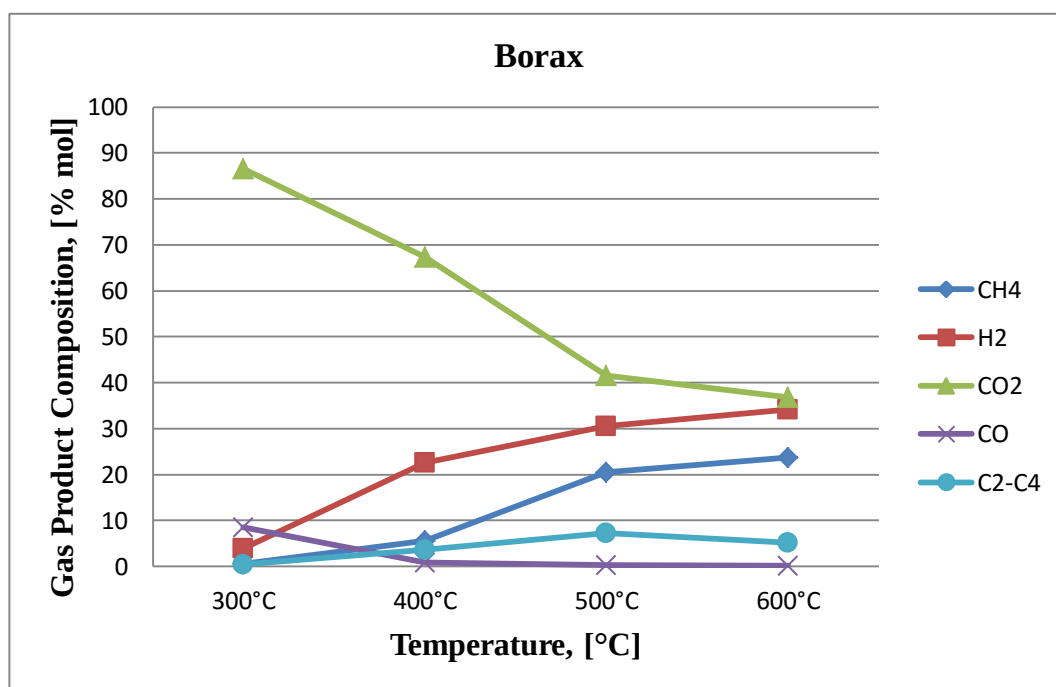


Figure 5.1.2.7 Gas composition of Red Kidney Bean Shells with Borax catalyst at different temperatures of sub- and supercritical water.

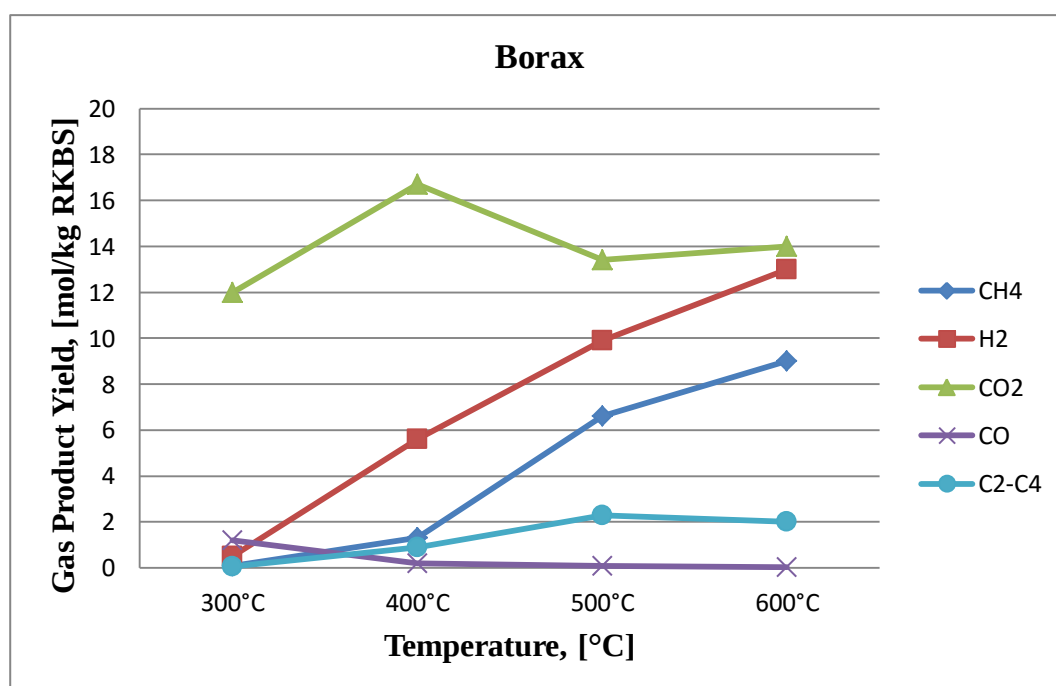


Figure 5.1.2.8 Gas product yield of Red Kidney Bean Shells with Borax catalyst at different temperatures of sub- and supercritical water.

The gas product yields of Red Kidney Bean Shells with Borax increased with increasing temperature as shown in Table 5.10 and Figures 5.1.2.7 and 5.1.2.8. The gas yields with Borax catalyst at 300°C, 400°C, 500°C and 600°C were found as 36.2, 59.8, 75.7 and 81.7 wt. % respectively (See Table 5.10). With increasing temperature from 300 to 600°C, mol % of H₂ increased sharply from 3.9 to 34.2, mol % of CH₄ rose continuously from 0.6 to 23.7 %. But, the mol % of CO₂ decreased sharply from 86.6 to 36.8 % with increasing temperature from 300°C to 600°C as expected and declined % mol of CO was found from 8.5 to 0.1 %. Additively, there was a C₂-C₄ % rising from 0.4 to 7.2 % mol at 300 to 500 °C whereas there was an decline from 7.2 to 5.2 at 500 to 600°C. Gas product yield of H₂ and CH₄ increased sharply, CO decreased slowly with increasing temperature. CO₂ yield increased between 300 and 400°C as 12.0 to 16.7 mol, however decreased from 16.7 to 13.4 mol between temperature 400 and 500°C and increased again slowly from 13.4 to 14.0 between temperature 500 and 600°C. Moles of C₂-C₄ increased slowly with increasing temperature until 500°C, although decreased at 600°C.

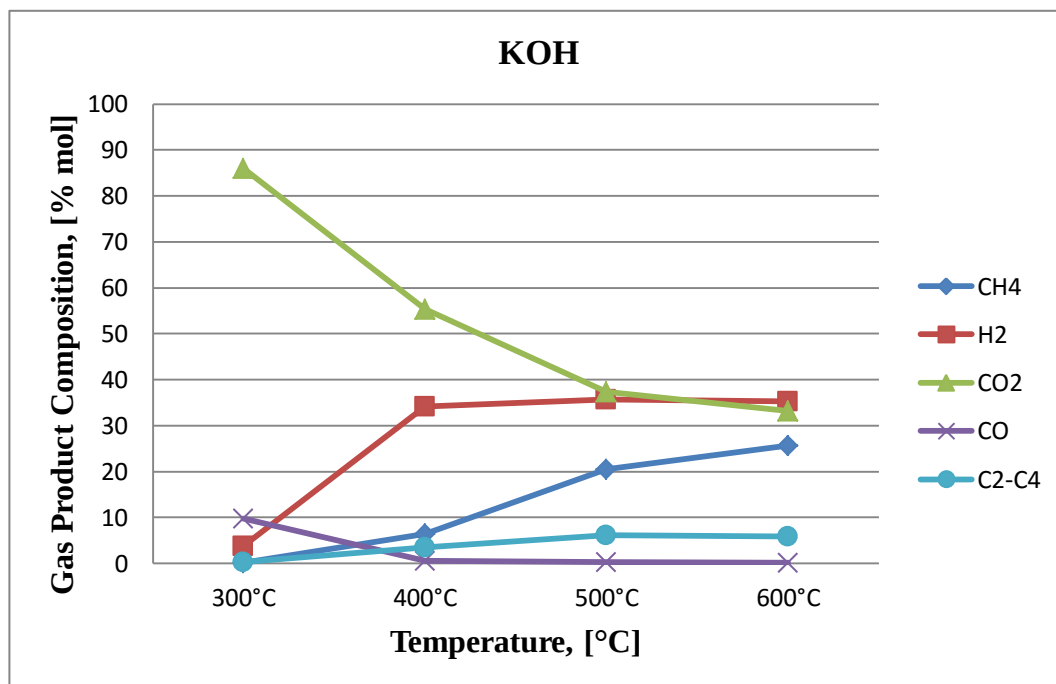


Figure 5.1.2.9 Gas composition of Red Kidney Bean Shells with KOH catalyst at different temperatures of sub- and supercritical water.

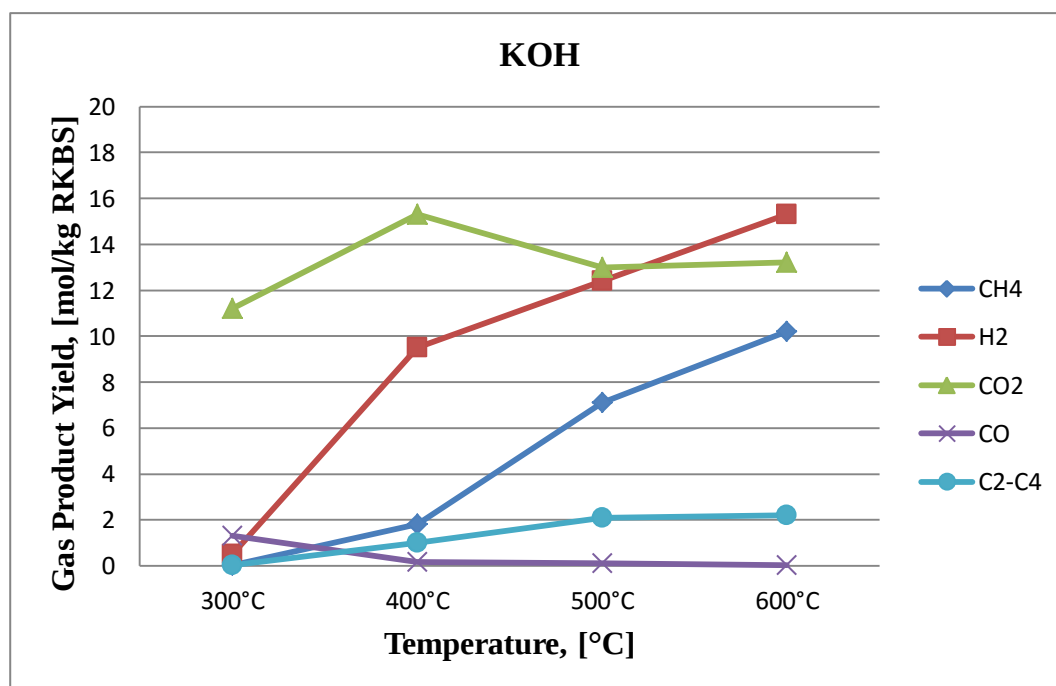


Figure 5.1.2.10 Gas product yield of Red Kidney Bean Shells with KOH catalyst at different temperatures of sub- and supercritical water.

A sharp increase of gas yield with KOH catalyst from 36.5 to 85.0 wt. % is seen in Table 5.11 with temperature increment from 300 to 600°C. Also, 57.6 and 74.5 wt. % values of gas yield were calculated for 400 and 500°C, respectively. It can be seen, gas yield rose with increasing temperature. Generally, the gas product yield increased, as temperature increased (See Figure 5.1.2.10). As it can be seen Table 5.11 and Figure 5.1.2.9, mol % of H₂ were found as 3.8, 34.2, 35.7, 35.2 % and mol % of CH₄ found as 0.2, 6.4, 20.5, 25.7 with rising temperature at 300, 400, 500, 600 °C, respectively. Here % of H₂ is crucial. Because, it increased sharply between 300-400°C while it was nearly same above 400°C counter to mineral catalysts (Like peapod with KOH). On the other hand, mol % of CO₂ fell suddenly as 86.0, 55.3, 37.3, 33.2, and mol % of CO decreased as 9.7, 0.6, 0.3, 0.1 with increasing temperature. According to the these results of CO, it dropped sharply between 300 and 400°C, before plunging down to a moderate decrease. Mol % of C₂-C₄ increased regularly between 300 – 500°C but decreased slightly at 600°C. Gas product yield of H₂ and CH₄ increased sharply, CO decreased slightly with increasing temperature. CO₂ yield increased between 300 – 400°C, decreased between 400 and 500°C, above 500°C it declined again. Moles of C₂-C₄ increased moderately with increasing temperature until 500°C, although decreased at 600°C.

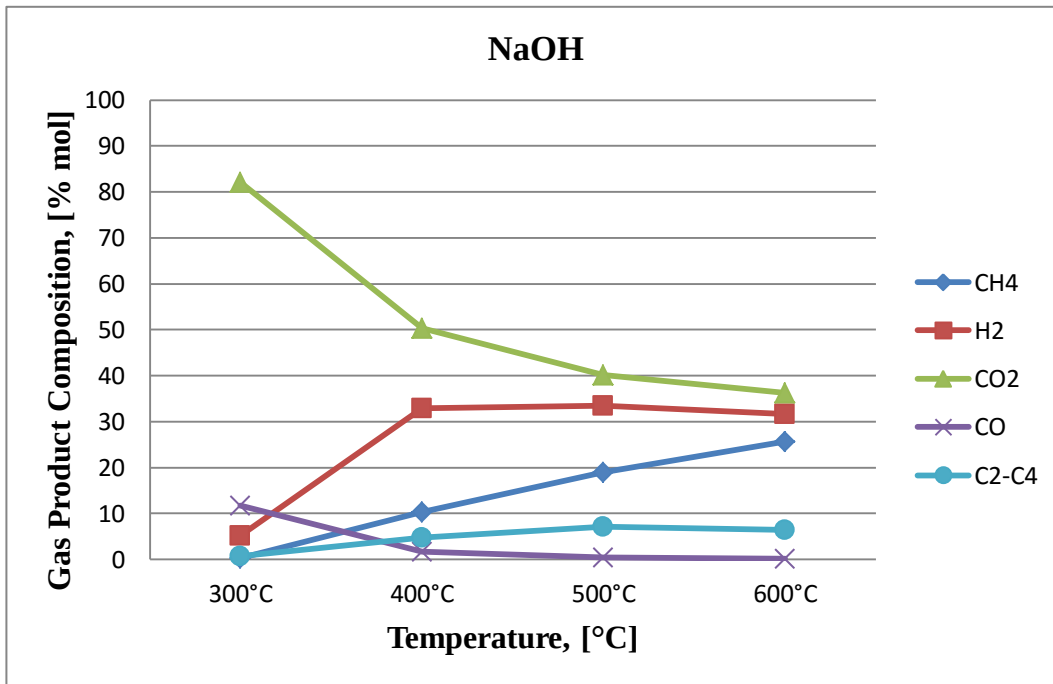


Figure 5.1.2.11 Gas composition of Red Kidney Bean Shells with NaOH catalyst at different temperatures of sub- and supercritical water.

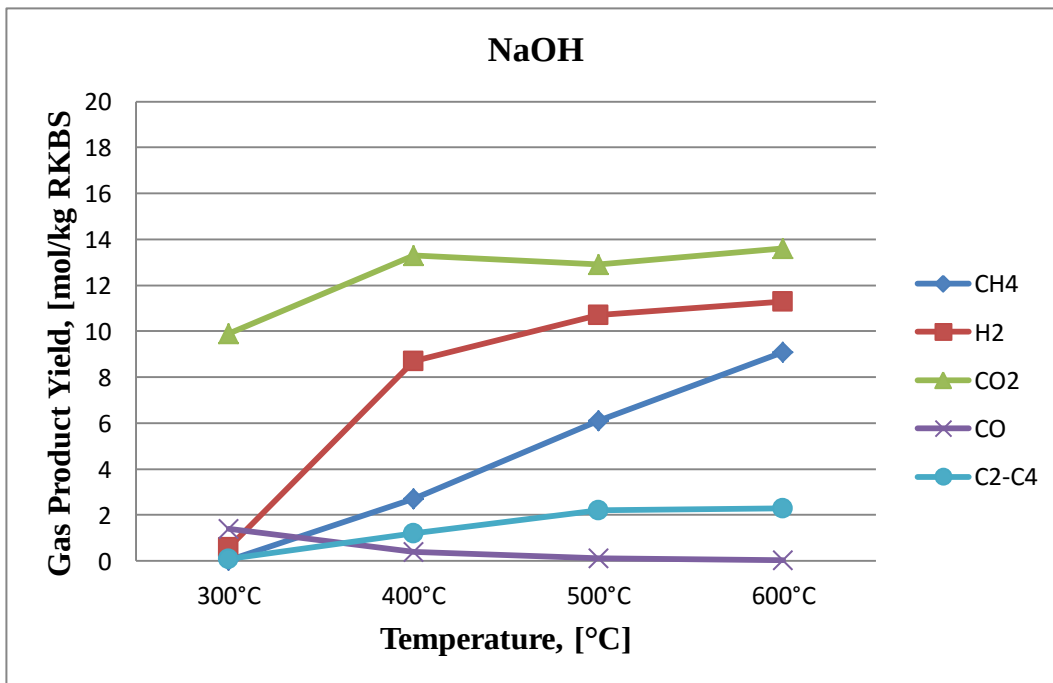


Figure 5.1.2.12 Gas product yield of Red Kidney Bean Shells with NaOH catalyst at different temperatures of sub- and supercritical water.

The gaseous products were 34.0, 57.5, 72.3 and 83.3 wt. % for four different temperature values (See Table 5.12). Figure 5.1.2.11 and 5.1.2.12 representing gas composition and gas yield. Mol % of H_2 rose generally from 5.2 to 31.6 % at 300 to 600°C. It increased sharply between 300-400°C while it decreased at temperatures from 500 to 600°C. And, mol % of CH_4 increased regularly from 0.3 to 25.7 mol %. Percentage of CO_2 and CO decreased with increasing temperature. Mol % of C_2-C_4 were 0.7, 4.8, 7.1, and 6.4 mol % for four different temperature values. As it can be seen the values rose until 500°C and then decreased as temperature increased from 500 to 600°C. Gas product yield of H_2 went up with decreasing slope especially after 400°C and CH_4 increased sharply, CO yield decreased slightly with increasing temperature. CO_2 yield fluctuated with increasing between 300 – 400°C, decreasing between 400 and 500°C and going up between 500 – 600°C again. Moles of C_2-C_4 increased moderately with increasing temperature.

5.2 Liquid Product Results

5.2.1 Total organic carbon (TOC) results

Table 5.2.1.1 TOC (ppm) of aqueous products of Peapod with and without catalyst at various temperature ranges for sub- and supercritical conditions.

Temperature Catalyst Type	300°C	400°C	500°C	600°C
No Catalyst	1730	1150	610	480
Trona	1780	1120	627	435
Dolomite	1580	1140	580	440
Borax	1800	1010	575	460
KOH	1765	1108	605	295
NaOH	1825	1210	550	315

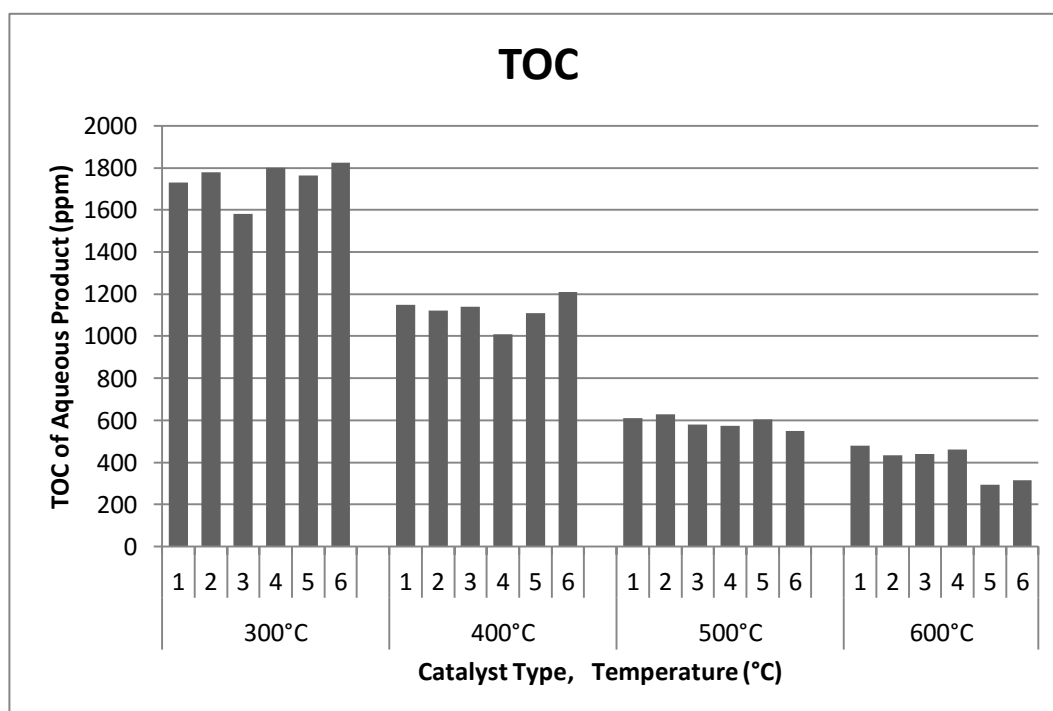


Figure 5.2.1.1 Variation of TOC of aqueous products with temperature and catalyst for SCWG of *peapod* (1: without catalyst, 2: Trona, 3: Dolomite, 4: Borax, 5: KOH, 6: NaOH).

Table 5.2.1.2 TOC (ppm) of aqueous products of Red Kidney Bean Shells with and without catalyst at various temperature ranges for sub- and supercritical conditions.

Catalyst Type \ Temperature	Temperature			
	300°C	400°C	500°C	600°C
No Catalyst	1780	1190	705	565
Trona	1800	1400	590	370
Dolomite	1600	1105	455	360
Borax	1720	980	480	415
KOH	1720	1150	610	375
NaOH	1950	1160	565	420

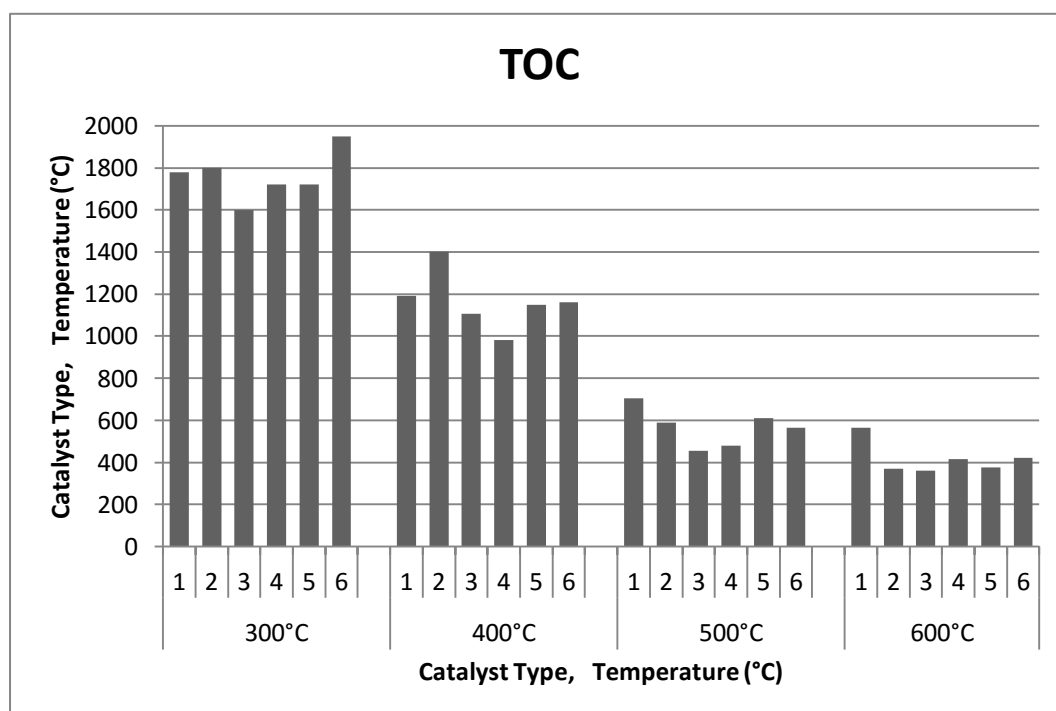


Figure 5.2.1.2 Variation of TOC of aqueous products with temperature and catalyst for SCWG of red kidney bean shells (1: without catalyst, 2: Trona, 3: Dolomite, 4: Borax, 5: KOH, 6: NaOH).

Total Organic Carbon Results of Peapod and Red Kidney Bean Shells were examined in Table 5.2.1.1 – Table 5.2.1.2 and Figure 5.2.1.1 – Figure 5.2.1.2. The values decreased with increasing temperature between 300 and 600°C. It can be understood from that biomass degradation was increasing with rising temperature. A large quantity of TOC values was obtained at subcritical (300°C) and supercritical conditions of water at 400°C. Although, it dropped sharply at SCW conditions of water at 500 and 600°C. The highest difference (1510 ppm) in TOC of peapod values between the 300°C – 600°C belonged to experiments with NaOH and the lowest one belonged to experiments with Dolomite (1140). Also, the greatest TOC difference of Red Kidney Bean Shells was occurred (1530 ppm) with NaOH catalyst again and minimum TOC difference (1215 ppm) was observed in the absence of catalyst.

5.2.2 High performance liquid chromatography (HPLC) results

The liquid products of SCWG contain variety of compounds and composition of main components. In this study, all of them were identified and measured by HPLC. There were carboxylic acids, furfurals, aldehydes, ketones in the aqueous phase. Compositions of each of them were given in Table 5.2.2.1.

Table 5.2.2.1 Quantitatively determined components by HPLC.

LIQUID PRODUCTS	
Carboxylic Acids	Glycolic Acid, Formic Acid, Acetic Acid
Furfurals	5-Methyl furfural, 5-Hydroxymethyl furfural, Furfural, 5-Methyl furfural
Aldehyde and Ketones	3-Methyl-2-cyclopenten-1-one, 2- Cyclopenten-1-one, Formaldehyde, Acetaldehyde, Acetone and propionaldehyde
Phenols	Phenol, m- and p-Cresols, o-Cresol, m- and p-Cresols, Catechol, 3-Metoxycatechol, Methoxybenzene and 4-methoxyphenol, 2-6 Dimethoxy phenol, 2-Methoxyphenol and 3- methoxyphenol, 4-Methyl guaiacol, 3,4 Dimethyl phenol, 4-Vinyl guaiacol, 3,5 Dimethyl phenol

Table 5.2.2.2 Variation of liquid product composition of peapod depends on temperature without catalyst in g/kg peapod.

No Catalyst					
Products		300°C	400°C	500°C	600°C
Total Carboxylic Acids	Glycolic Acid	13.44	2.66	23.17	12.23
	Formic Acid	22.51	21.08	18.44	5.80
	Acetic Acid	17.60	29.94	6.77	9.39
Total Furfurals	5-Methyl furfural	17.85	23.40	8.60	18.91
	1,4 Dioxan	9.15	14.39	0.34	3.06
	Furfural	0.97	0.06	0.10	0.46
Total aldehyde and Ketones	3-Methyl-2-cyclopenten-1-one	0.18	0.10	0.02	0.01
	2-Cyclopenten-1-on	0.07	0.63	0.07	0.20
	Formaldehyde	0.37	0.41	0.20	0.55
	Acetaldehyde	0.21	0.01	<0.01	0.01
	Acetone and Propionaldehyde	0.02	0.07	<0.01	<0.01
Total Phenols	Phenol	0.03	0.01	0.01	<0.01
	m- and p-Cresol	0.71	0.57	0.39	<0.01
	o-Cresol	0.11	0.00	1.84	<0.01
	Resorcinol	0.58	0.82	1.21	0.13
	Catechol	0.17	0.24	0.27	0.03
	3-Methoxycatechol	0.11	0.16	0.01	0.04
	Metoxybenzene and 4-methoxyphenol	1.45	4.33	0.03	0.09
	2-6 Dimethoxy phenol	0.33	0.07	0.00	0.18
	2-Methoxy phenol and 3-methoxy phenol	0.25	0.07	0.01	<0.01
	4-Methyl guaiacol	0.21	0.12	0.08	0.05
	3,4 Dimethyl phenol	0.19	0.82	0.95	0.07
	4-Vinyl guaiacol	0.07	0.37	0.49	<0.01
	3,5 Dimethyl phenol	<0.01	0.22	1.27	0.18

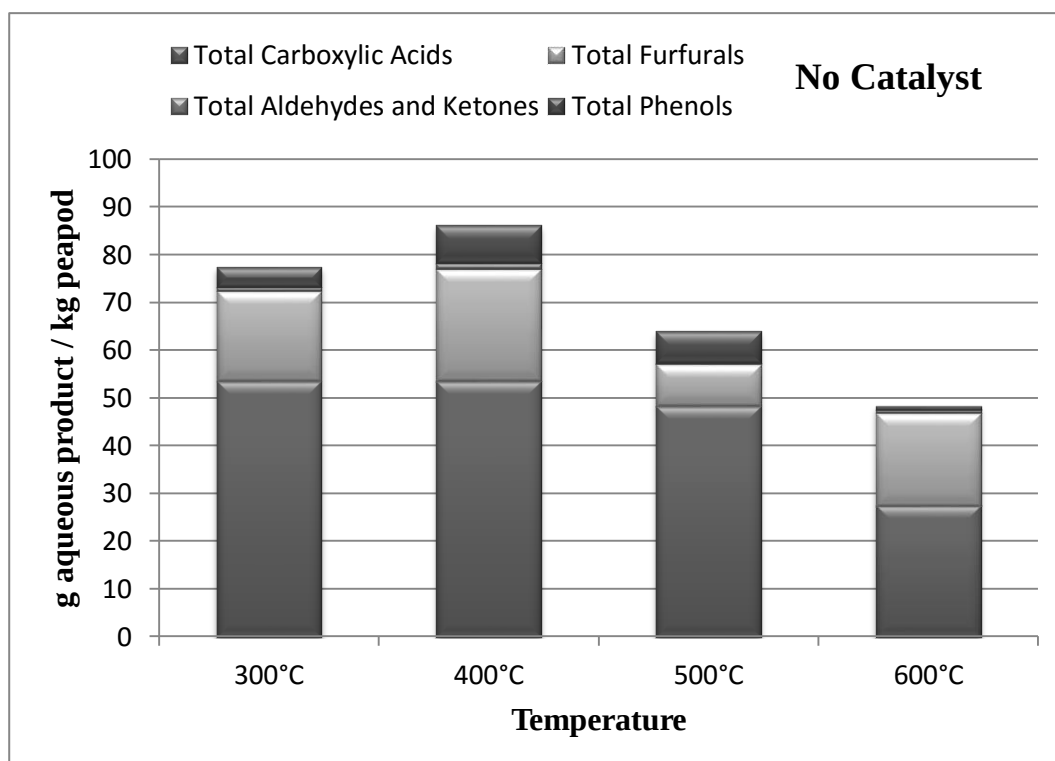


Figure 5.2.2.1 Composition of aqueous product for 4 main group at different temperatures of peapod without catalyst.

Variation of peapod liquid product composition and results of total carboxylic acid, total furfurals total aldehydes and ketones and total phenols without catalyst is shown in Table 5.2.2.2 and Figure 5.2.2.1, respectively. Total carboxylic acids and total phenols increased with increasing temperature from 300 to 400°C, above 400°C it decreased. Total furfurals aldehydes and ketones increased between 300 – 400°C, decreased between 400 and 500°C, above 500°C it rose again. At 300°C, Total carboxylic acids was the highest yield with 53.55 g/kg peapod. At 600°C, 5-Methyl furfural had highest concentration in liquid products with 18.91 g.

Table 5.2.2.3 Variation of liquid product composition of peapod depends on temperature with Trona in g/kg peapod.

Trona					
Products		300°C	400°C	500°C	600°C
Total Carboxylic Acids	Glycolic Acid	12.32	14.66	17.91	8.77
	Formic Acid	2.47	3.78	4.49	33.80
	Acetic Acid	56.57	41.10	8.52	12.17
Total Furfurals	5-Methyl furfural	46.78	14.99	11.81	2.48
	1,4 Dioxan	27.17	26.69	4.27	0.18
	Furfural	0.18	0.16	0.14	0.01
Total aldehyde and Ketones	3-Methyl-2-cyclopenten-1-one	0.25	0.02	0.03	<0.01
	2-Cyclopenten-1-on	0.91	0.34	0.26	0.00
	Formaldehyde	0.32	0.27	0.23	0.05
	Acetaldehyde	0.02	0.06	0.03	<0.01
	Acetone and Propionaldehyde	0.02	<0.01	<0.01	<0.01
Total Phenols	Phenol	<0.01	<0.01	0.03	<0.01
	m- and p-Cresol	0.13	<0.01	0.39	0.12
	o-Cresol	1.08	0.21	0.13	0.00
	Resorcinol	1.05	0.70	3.67	0.02
	Catechol	0.69	0.25	0.10	<0.01
	3-Methoxycatechol	0.39	0.19	0.16	0.02
	Metoxybenzene and 4-methoxyphenol	2.19	0.21	0.09	0.15
	2-6 Dimethoxy phenol	0.37	0.08	0.01	0.12
	2-Methoxy phenol and 3-methoxy phenol	0.32	0.15	0.02	0.01
	4-Methyl guaiacol	0.54	0.30	0.03	0.35
	3,4 Dimethyl phenol	0.56	0.98	0.05	0.04
	4-Vinyl guaiacol	0.03	0.67	0.49	0.01
	3,5 Dimethyl phenol	0.15	0.27	1.27	0.34

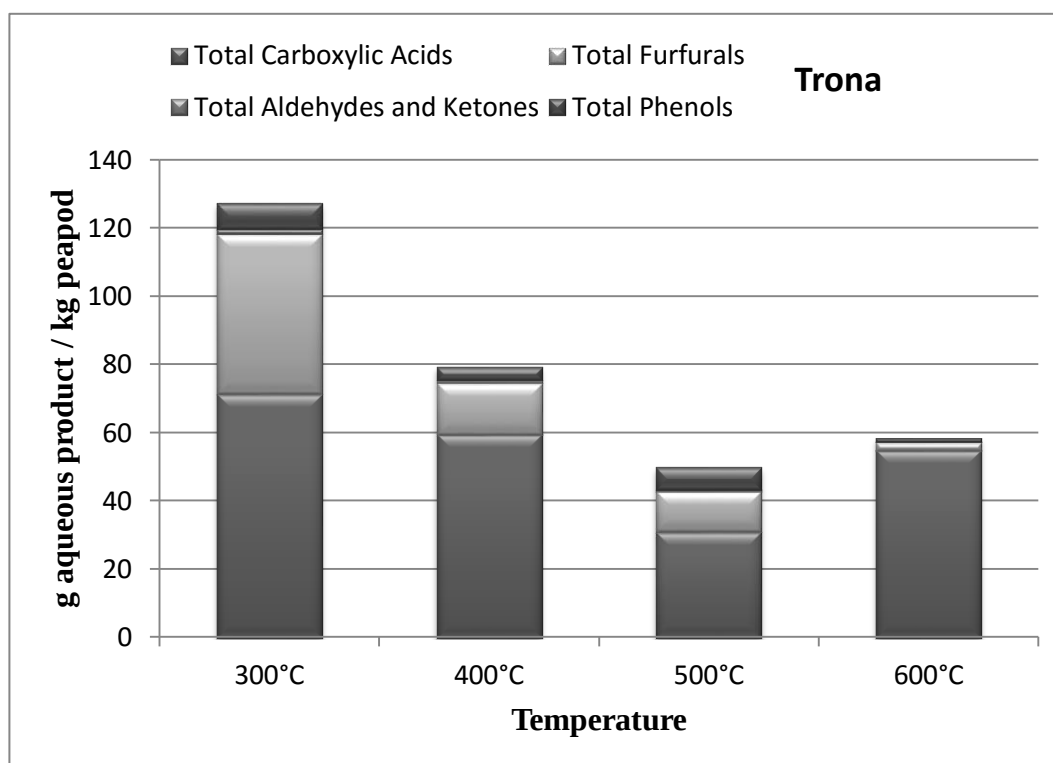


Figure 5.2.2.2 Composition of aqueous product for 4 main group at different temperatures of peapod with Trona.

Table 5.2.2.3 and Figure 5.2.2.2 gives change of aqueous products for Trona experiments with respect to temperature. Total aldehydes and ketones and total furfurals dropped sharply with temperature increment. Total carboxylic acids decreased until 500°C and then increased when temperature increased from 500 to 600°C. Total phenols fluctuated with decreasing between 300 – 400°C, increasing between 400 and 500°C and declining between 500-600°C again. At 300°C, Total carboxylic acids was the highest yield with 71.35 g/kg peapod. Formic acid had highest concentration in liquid products with 33.80 for 600°C .

Table 5.2.2.4 Variation of liquid product composition of peapod depends on temperature with Dolomite in g/kg peapod.

Dolomite					
Products		300°C	400°C	500°C	600°C
Total Carboxylic Acids	Glycolic Acid	4.75	3.14	31.49	2.23
	Formic Acid	6.48	16.06	21.05	19.05
	Acetic Acid	35.90	12.48	5.51	25.11
Total Furfurals	5-Methyl furfural	22.55	16.09	13.37	2.21
	1,4 Dioxan	16.29	18.24	10.13	2.06
	Furfural	1.03	0.14	0.12	0.01
Total aldehyde and Ketones	3-Methyl-2-cyclopenten-1-one	0.11	0.05	0.06	<0.01
	2-Cyclopenten-1-on	1.11	0.54	0.05	0.01
	Formaldehyde	0.17	0.06	0.02	0.08
	Acetaldehyde	0.45	0.11	<0.01	0.01
	Acetone and Propionaldehyde	0.06	0.01	<0.01	0.01
Total Phenols	Phenol	<0.01	<0.01	0.01	<0.01
	m- and p-Cresol	0.70	0.79	0.25	<0.01
	o-Cresol	0.00	0.96	0.02	<0.01
	Resorcinol	0.88	0.61	0.63	0.03
	Catechol	0.49	0.41	0.17	<0.01
	3-Methoxycatechol	0.12	0.14	0.04	0.02
	Metoxybenzene and 4-methoxyphenol	1.31	2.74	0.05	0.15
	2-6 Dimethoxy phenol	0.30	0.18	<0.01	0.01
	2-Methoxy phenol and 3-methoxy phenol	0.28	0.10	0.02	0.01
	4-Methyl guaiacol	0.34	0.31	0.01	<0.01
	3,4 Dimethyl phenol	0.32	0.79	1.07	<0.01
	4-Vinyl guaiacol	0.13	0.53	0.44	0.18
	3,5 Dimethyl phenol	0.01	0.22	0.06	0.34

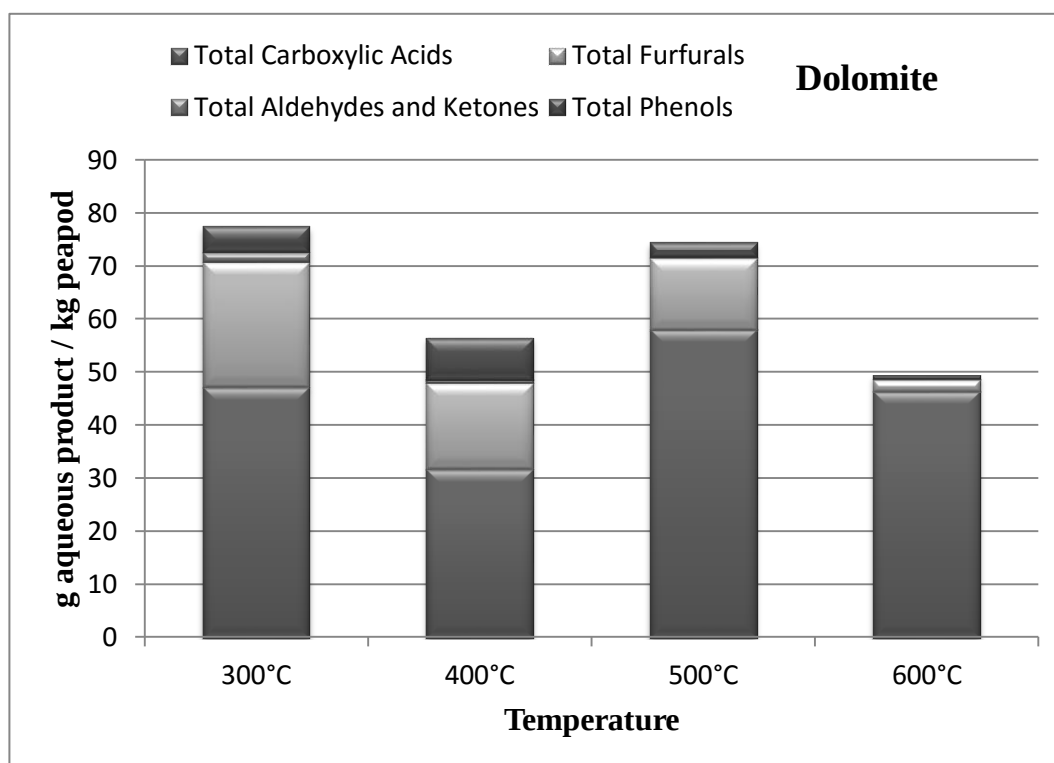


Figure 5.2.2.3 Composition of aqueous product for 4 main group at different temperatures of peapod with Dolomite.

According to Table 5.2.2.4 and Figure 5.2.2.3, there were total aldehydes and ketones and total furfurals decrease with increasing temperature for Dolomite catalyst. Additively, there was total phenols rising from 300°C to 400°C whereas there was an decline at 400 to 600°C. Total carboxylic acids decreased between 300 – 400°C, increased between 400 and 500°C, above 500°C it declined again. At 300°C, Total carboxylic acids was the highest yield with 47.13 g/kg peapod. At 600°C, Acetic acid had highest concentration in liquid products with 18.91 g.

Table 5.2.2.5 Variation of liquid product composition of peapod depends on temperature with Borax in g/kg peapod.

Borax					
Products		300°C	400°C	500°C	600°C
Total Carboxylic Acids	Glycolic Acid	20.26	8.95	11.05	6.63
	Formic Acid	4.41	3.92	7.25	24.44
	Acetic Acid	38.02	31.13	7.11	7.28
Total Furfurals	5-Methyl furfural	24.86	7.71	22.30	9.20
	1,4 Dioxan	9.53	5.30	7.10	1.44
	Furfural	0.09	0.07	0.06	0.01
Total aldehyde and Ketones	3-Methyl-2-cyclopenten-1-one	0.20	0.02	0.01	<0.01
	2-Cyclopenten-1-on	1.13	0.82	0.04	0.01
	Formaldehyde	0.16	0.10	0.06	0.10
	Acetaldehyde	0.07	0.01	0.01	0.01
	Acetone and Propionaldehyde	<0.01	0.01	<0.01	0.01
Total Phenols	Phenol	0.01	0.01	0.02	<0.01
	m- and p-Cresol	0.62	1.50	0.43	0.12
	o-Cresol	1.11	<0.01	0.03	0.18
	Resorcinol	0.55	0.34	0.90	0.02
	Catechol	0.53	0.12	0.45	<0.01
	3-Methoxycatechol	0.41	0.10	0.10	0.03
	Metoxybenzene and 4-methoxyphenol	1.93	0.48	0.24	0.11
	2-6 Dimethoxy phenol	0.34	0.04	0.19	0.01
	2-Methoxy phenol and 3-methoxy phenol	0.25	0.02	0.08	<0.01
	4-Methyl guaiacol	0.48	0.03	0.25	<0.01
	3,4 Dimethyl phenol	0.55	0.41	1.00	0.02
	4-Vinyl guaiacol	0.17	0.33	0.57	<0.01
	3,5 Dimethyl phenol	0.14	<0.01	0.19	0.19

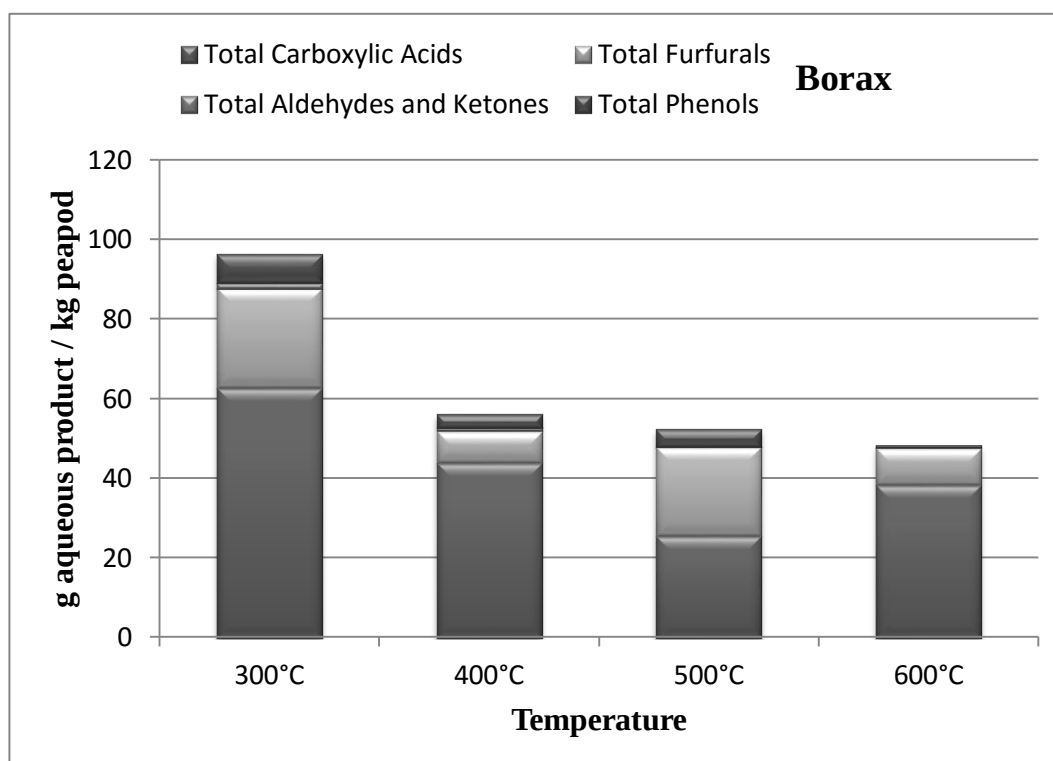


Figure 5.2.2.4 Composition of aqueous product for 4 main group at different temperatures of peapod with Borax.

Variation of peapod liquid product composition and results of total carboxylic acid, total furfurals total aldehydes and ketones and total phenols with Borax is examined in Table 5.2.2.5 and Figure 5.2.2.4, respectively. Total carboxylic acids and total aldehydes-ketones decreased sharply with increasing temperature, whereas it tended to increase between 500 and 600°C. Total phenols and total furfurals decreased between 300 – 400°C, increased between 400 and 500°C, above 500°C it went up again. At 300°C, Total carboxylic acids was the highest yield with 62.69 g/kg peapod. Formic acid had highest concentration in liquid products, too like Trona with 24.44 g. for 600°C.

Table 5.2.2.6 Variation of liquid product composition of peapod depends on temperature with KOH in g/kg peapod.

KOH					
Products		300°C	400°C	500°C	600°C
Total Carboxylic Acids	Glycolic Acid	16.84	24.05	20.54	23.83
	Formic Acid	0.24	8.00	2.30	0.20
	Acetic Acid	40.95	3.77	2.04	3.80
Total Furfurals	5-Methyl furfural	<0.01	26.49	4.31	<0.01
	1,4 Dioxan	11.36	13.60	0.07	<0.01
	Furfural	0.01	0.02	0.01	<0.01
Total aldehyde and Ketones	3-Methyl-2-cyclopenten-1-one	0.01	<0.01	<0.01	<0.01
	2-Cyclopenten-1-on	<0.01	0.16	0.40	<0.01
	Formaldehyde	0.20	0.20	0.11	0.06
	Acetaldehyde	0.05	0.04	0.00	0.01
	Acetone and Propionaldehyde	0.20	0.20	0.28	<0.01
Total Phenols	Phenol	<0.01	0.01	0.02	<0.01
	m- and p-Cresol	<0.01	0.13	0.11	0.23
	o-Cresol	<0.01	0.14	<0.01	<0.01
	Resorcinol	10.96	0.21	0.67	0.01
	Catechol	3.26	0.66	0.07	<0.01
	3-Methoxycatechol	19.62	0.10	0.30	0.03
	Metoxybenzene and 4-methoxyphenol	2.97	1.55	0.67	0.03
	2-6 Dimethoxy phenol	<0.01	0.11	0.19	<0.01
	2-Methoxy phenol and 3-methoxy phenol	<0.01	0.13	0.14	<0.01
	4-Methyl guaiacol	<0.01	0.28	0.02	0.02
	3,4 Dimethyl phenol	<0.01	0.63	1.10	<0.01
	4-Vinyl guaiacol	<0.01	0.09	0.58	0.01
	3,5 Dimethyl phenol	<0.01	0.06	0.03	0.00

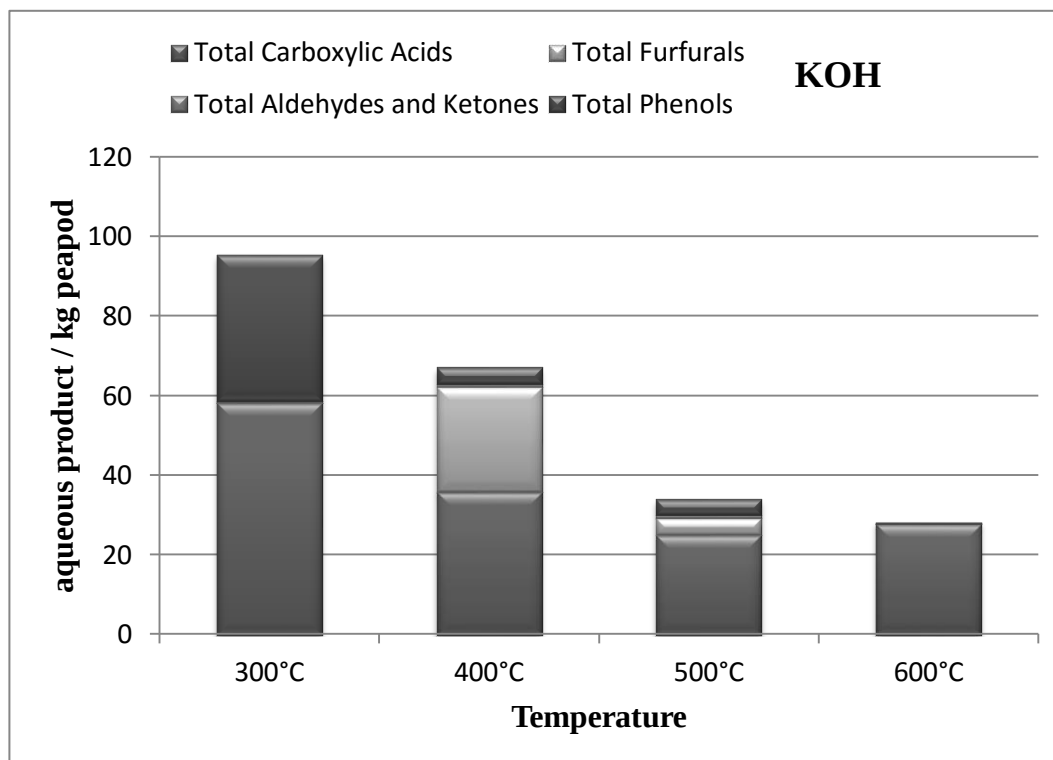


Figure 5.2.2.5 Composition of aqueous product for 4 main group at different temperatures of peapod with KOH.

Table 5.2.2.6 and Figure 5.2.2.5 gives change of aqueous products for KOH experiments with respect to temperature. Total phenols decreased dramatically with temperature from 300 to 400°C, and it was sustaining to decline slowly above 400°C. Total carboxylic acids decreased until 500°C and then increased when temperature increased from 500 to 600°C. Total furfurals went up strongly from temperature 300 to 400°C and declined dramatically from temperature 400 to 600°C up to zero value at 600°C. Total aldehydes and ketones increased until 500°C and then decreased sharply when temperature increased from 500 to 600°C. At 300°C, Total carboxylic acids was the highest yield with 58.03 g/kg peapod. At 600°C, Glycolic acid had highest concentration in liquid products with 23.83 g.

Table 5.2.2.7 Variation of liquid product composition of peapod depends on temperature with NaOH in g/kg peapod.

NaOH					
Products		300°C	400°C	500°C	600°C
Total Carboxylic Acids	Glycolic Acid	0.14	7.49	5.21	0.00
	Formic Acid	22.99	21.92	1.55	1.07
	Acetic Acid	3.38	14.69	29.63	5.18
Total Furfurals	5-Methyl furfural	1.16	25.32	4.02	<0.01
	1,4 Dioxan	4.64	14.19	10.97	20.79
	Furfural	<0.01	0.04	0.03	<0.01
Total aldehyde and Ketones	3-Methyl-2-cyclopenten-1-one	<0.01	<0.01	<0.01	0.04
	2-Cyclopenten-1-on	<0.01	0.11	<0.01	<0.01
	Formaldehyde	0.19	0.18	0.12	0.02
	Acetaldehyde	0.02	<0.01	<0.01	<0.01
	Acetone and Propionaldehyde	0.04	0.02	<0.01	<0.01
Total Phenols	Phenol	<0.01	0.02	0.01	<0.01
	m- and p-Cresol	0.18	<0.01	0.02	0.15
	o-Cresol	<0.01	<0.01	<0.01	<0.01
	Resorcinol	<0.01	0.14	0.43	0.01
	Catechol	<0.01	0.08	0.04	<0.01
	3-Methoxycatechol	0.07	0.12	0.32	0.10
	Metoxybenzene and 4-methoxyphenol	0.21	2.51	2.12	0.13
	2-6 Dimethoxy phenol	0.07	0.15	0.31	0.02
	2-Methoxy phenol and 3-methoxy phenol	0.03	0.25	0.12	0.33
	4-Methyl guaiacol	0.18	0.28	0.23	0.10
	3,4 Dimethyl phenol	0.02	0.57	1.09	<0.01
	4-Vinyl guaiacol	<0.01	0.02	0.88	<0.01
	3,5 Dimethyl phenol	<0.01	0.04	<0.01	0.19

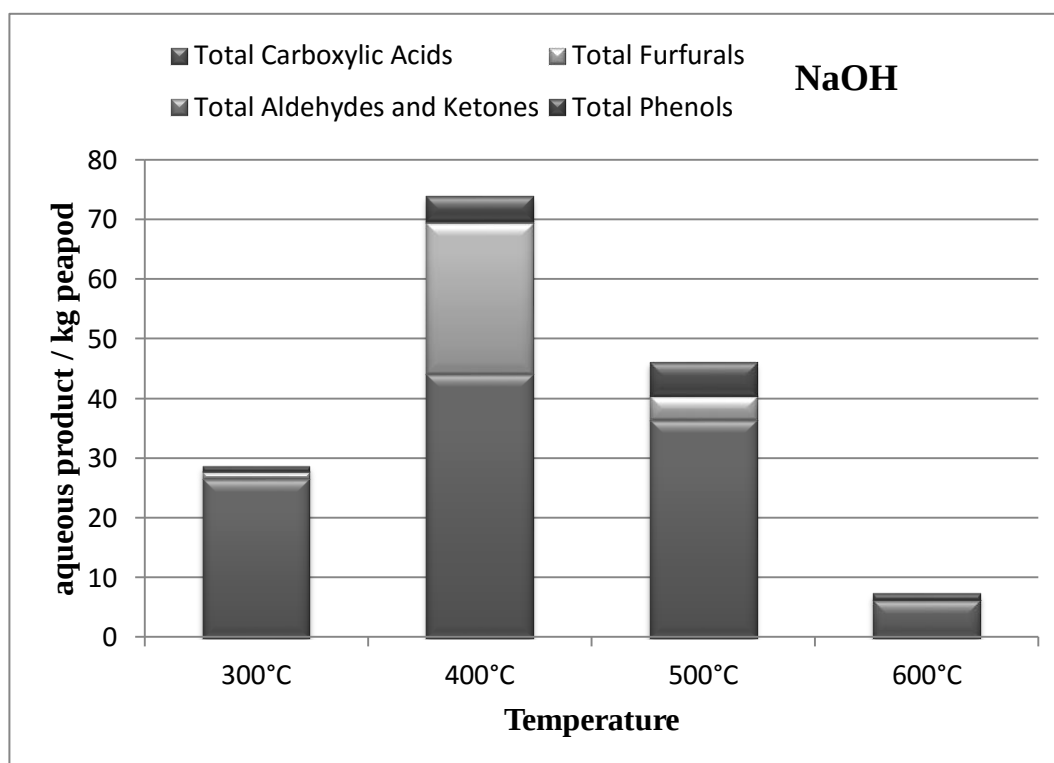


Figure 5.2.2.6 Composition of aqueous product for 4 main group at different temperatures of peapod with NaOH.

According to Table 5.2.2.7 and Figure 5.2.2.6, there were total aldehydes and ketones and total furfurals decrease with increasing temperature for NaOH catalyst. Total carboxylic acids and total aldehydes-ketones increased between 300 – 400°C, decreased between 400 and 600°C. Total furfurals rise sharply from temperature 300 to 400°C and decreased steeply from temperature 400 to 600°C up to zero value at 600°C just like behavior of KOH. Total phenols increased until 500°C and then declined suddenly, when temperature increased from 500 to 600°C. At 300°C, Total carboxylic acids was the highest yield with 26.11 g/kg peapod. 1,4 Dioxan had highest concentration in liquid products too with 20.79 g. for 600°C.

Table 5.2.2.8 Variation of liquid product composition of RKBS depends on temperature without catalyst in g/kg RKBS.

No Catalyst					
Products		300°C	400°C	500°C	600°C
Total Carboxylic Acids	Glycolic Acid	4.88	0.12	7.8	18.29
	Formic Acid	22.90	10.49	4.04	32.58
	Acetic Acid	8.97	6.68	5.45	5.41
Total Furfurals	5-Methyl furfural	5.96	11.04	9.17	1.46
	1,4 Dioxan	3.09	15.37	17.25	7.29
	Furfural	0.04	0.02	0.01	<0.01
Total aldehyde and Ketones	3-Methyl-2-cyclopenten-1-one	0.02	0.01	0.01	<0.01
	2-Cyclopenten-1-on	0.72	0.06	0.06	0.02
	Formaldehyde	0.31	0.22	0.17	0.27
	Acetaldehyde	0.09	0.03	0.04	0.07
	Acetone and Propionaldehyde	0.04	0.15	0.15	0.01
Total Phenols	Phenol	<0.01	0.03	0.03	0.01
	m- and p-Cresol	0.14	0.04	0.04	<0.01
	o-Cresol	0.02	0.33	0.33	<0.01
	Resorcinol	0.53	0.22	0.06	<0.01
	Catechol	0.16	0.09	0.03	0.01
	3-Methoxycatechol	0.14	0.21	0.08	0.08
	Metoxybenzene and 4-methoxyphenol	1.53	3.02	0.07	0.33
	2-6 Dimethoxy phenol	0.27	0.35	0.01	0.01
	2-Methoxy phenol and 3-methoxy phenol	0.27	0.04	0.01	0.30
	4-Methyl guaiacol	0.02	0.43	0.03	0.12
	3,4 Dimethyl phenol	0.07	0.90	1.24	<0.01
	4-Vinyl guaiacol	0.04	0.70	0.60	<0.01
	3,5 Dimethyl phenol	0.02	0.33	0.07	<0.01

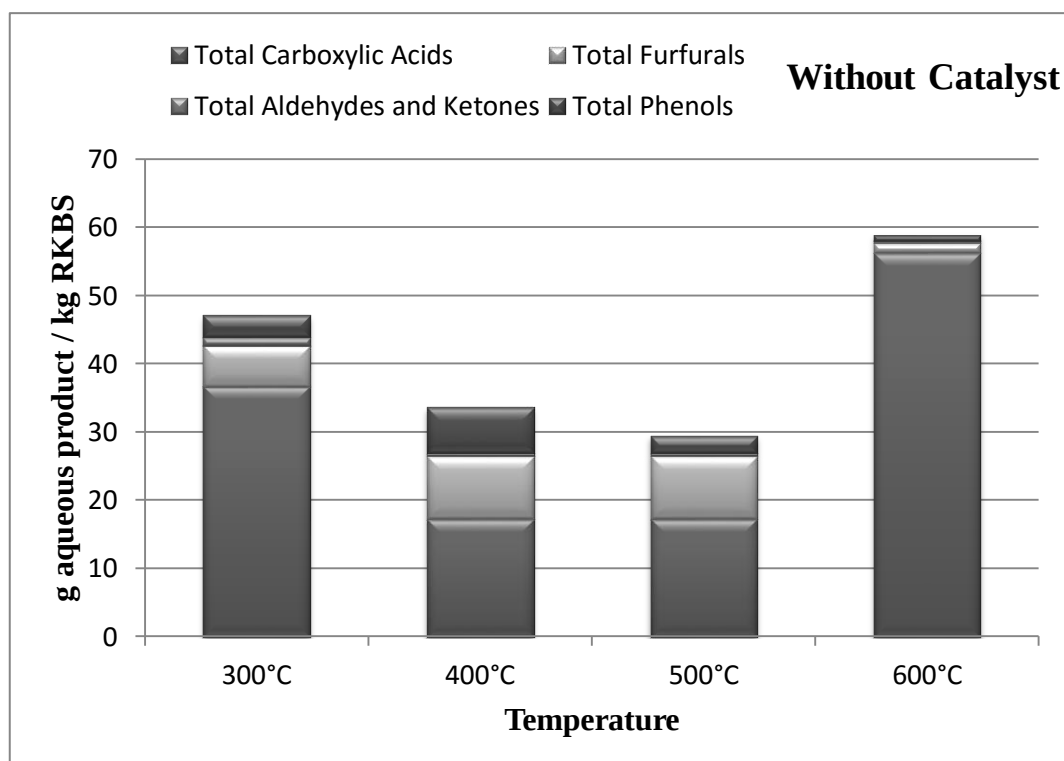


Figure 5.2.2.7 Composition of aqueous product for 4 main group at different temperatures of RKBS without catalyst.

Variation of RKBS liquid product composition and results of total carboxylic acid, total furfurals total aldehydes and ketones and total phenols without catalyst is shown in Table 4.2.2.8 and Figure 4.2.2.7, respectively. Total aldehydes declined with increasing temperature. Total carboxylic acids decreased between 300 – 400°C, remained steady between 400 and 500°C, above 500°C it rose. Total furfurals increased between 300 – 400°C, remained steady between 400 and 500°C, above 500°C it decreased. Total phenols rose until 400°C and then decreased continuously when temperature increased from 400 to 600°C. At 300°C, Total carboxylic acids was the highest yield with 36.74 g/kg RKBS. At 600°C, Formic acid had highest concentration in liquid products with 32.58 g.

Table 5.2.2.9 Variation of liquid product composition of RKBS depends on temperature with Trona in g/kg RKBS.

Trona					
Products		300°C	400°C	500°C	600°C
Total Carboxylic Acids	Glycolic Acid	9.30	8.26	8.03	8.97
	Formic Acid	27.59	3.49	8.72	3.68
	Acetic Acid	10.32	31.90	2.18	18.20
Total Furfurals	5-Methyl furfural	24.22	7.22	43.25	<0.01
	1,4 Dioxan	17.80	4.63	6.68	<0.01
	Furfural	0.10	0.02	0.02	<0.01
Total aldehyde and Ketones	3-Methyl-2-cyclopenten-1-one	0.11	0.02	<0.01	<0.01
	2-Cyclopenten-1-on	0.38	0.24	0.14	0.05
	Formaldehyde	0.27	0.13	0.51	0.08
	Acetaldehyde	0.11	0.00	0.14	<0.01
	Acetone and Propionaldehyde	0.07	0.13	0.15	0.01
Total Phenols	Phenol	0.03	0.00	0.01	<0.01
	m- and p-Cresol	0.11	0.25	0.05	0.05
	o-Cresol	0.13	0.72	<0.01	<0.01
	Resorcinol	0.27	0.25	0.07	0.01
	Catechol	0.57	0.08	0.01	<0.01
	3-Methoxycatechol	0.17	0.04	0.11	0.08
	Metoxybenzene and 4-methoxyphenol	3.52	0.70	0.85	0.14
	2-6 Dimethoxy phenol	0.33	0.00	0.04	0.02
	2-Methoxy phenol and 3-methoxy phenol	0.33	0.02	0.05	<0.01
	4-Methyl guaiacol	0.44	0.12	0.01	0.09
	3,4 Dimethyl phenol	0.11	0.25	1.09	<0.01
	4-Vinyl guaiacol	0.03	0.46	0.20	<0.01
	3,5 Dimethyl phenol	<0.01	0.01	0.05	<0.01

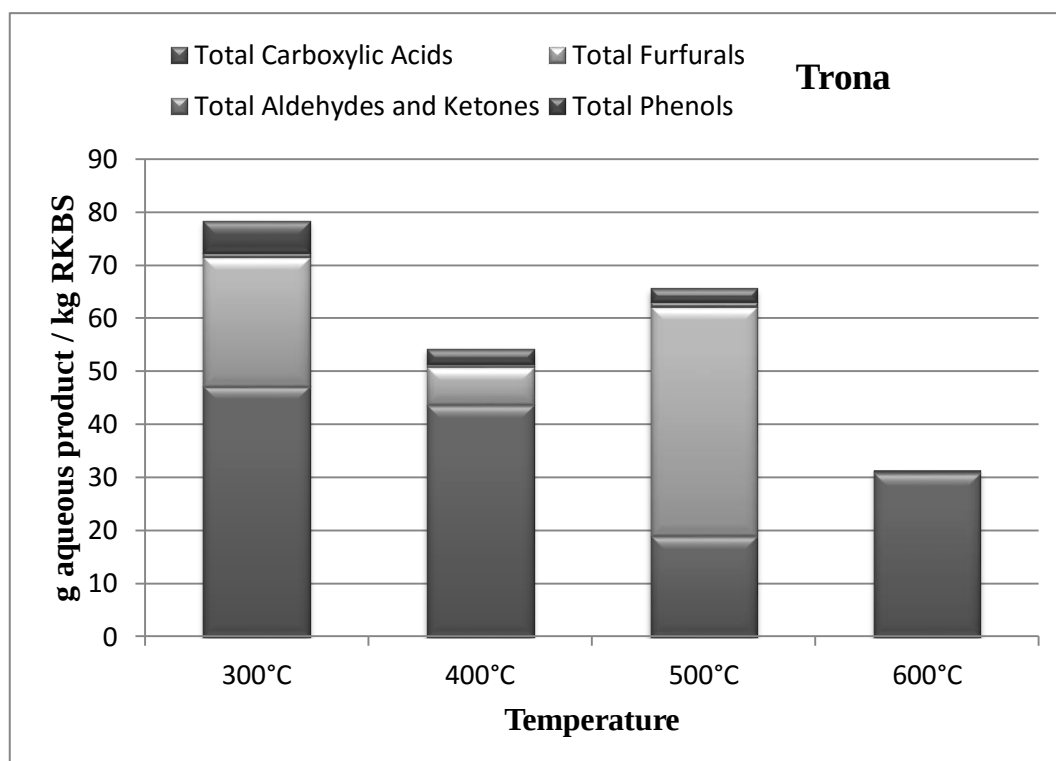


Figure 5.2.2.8 Composition of aqueous product for 4 main group at different temperatures of RKBS with Trona.

Table 4.2.2.9 and Figure 4.2.2.8 gives change of aqueous products for Trona experiments with respect to temperature. Total phenols dropped sharply with temperature increment. Total carboxylic acids decreased until 500°C and then increased when temperature increased from 500 to 600°C. Total furfurals fluctuated with decreasing suddenly between 300 – 400°C, increasing more sudden between 400 and 500°C and declining to nearly zero value between 500 – 600°C again. Total aldehydes and ketones decreased slightly between 300 – 400°C, went up to the value of 300°C between 400 and 500°C, above 500°C it decreased again. At 300°C, Total carboxylic acids was the highest yield with 47.21 g/kg RKBS. Acetic acid had highest concentration in liquid products with 18.20 for 600°C .

Table 5.2.2.10 Variation of liquid product composition of RKBS depends on temperature with Dolomite in g/kg RKBS.

Dolomite					
Products		300°C	400°C	500°C	600°C
Total Carboxylic Acids	Glycolic Acid	25.98	0.52	8.97	20.01
	Formic Acid	8.02	1.44	18.01	1.81
	Acetic Acid	25.26	9.65	6.33	11.47
Total Furfurals	5-Methyl furfural	1.53	11.69	2.13	0.78
	1,4 Dioxan	29.30	6.18	5.69	5.92
	Furfural	0.05	0.03	0.01	<0.01
Total aldehyde and Ketones	3-Methyl-2-cyclopenten-1-one	0.03	0.05	0.03	<0.01
	2-Cyclopenten-1-on	0.83	0.42	0.03	20.01
	Formaldehyde	0.34	0.21	0.19	0.39
	Acetaldehyde	0.02	0.23	0.03	0.10
	Acetone and Propionaldehyde	0.06	0.14	0.13	<0.01
Total Phenols	Phenol	0.03	<0.01	<0.01	<0.01
	m- and p-Cresol	0.03	0.02	0.02	0.02
	o-Cresol	0.81	0.01	6.78	0.00
	Resorcinol	0.61	0.05	0.02	1.81
	Catechol	0.09	0.06	0.01	11.47
	3-Methoxycatechol	0.16	0.10	0.19	0.78
	Metoxybenzene and 4-methoxyphenol	1.23	2.14	0.92	<0.01
	2-6 Dimethoxy phenol	0.31	0.10	0.39	<0.01
	2-Methoxy phenol and 3-methoxy phenol	0.29	0.25	0.19	0.18
	4-Methyl guaiacol	0.28	0.32	1.92	<0.01
	3,4 Dimethyl phenol	0.08	0.81	1.65	0.02
	4-Vinyl guaiacol	<0.01	0.65	0.56	<0.01
	3,5 Dimethyl phenol	0.01	0.27	0.18	<0.01

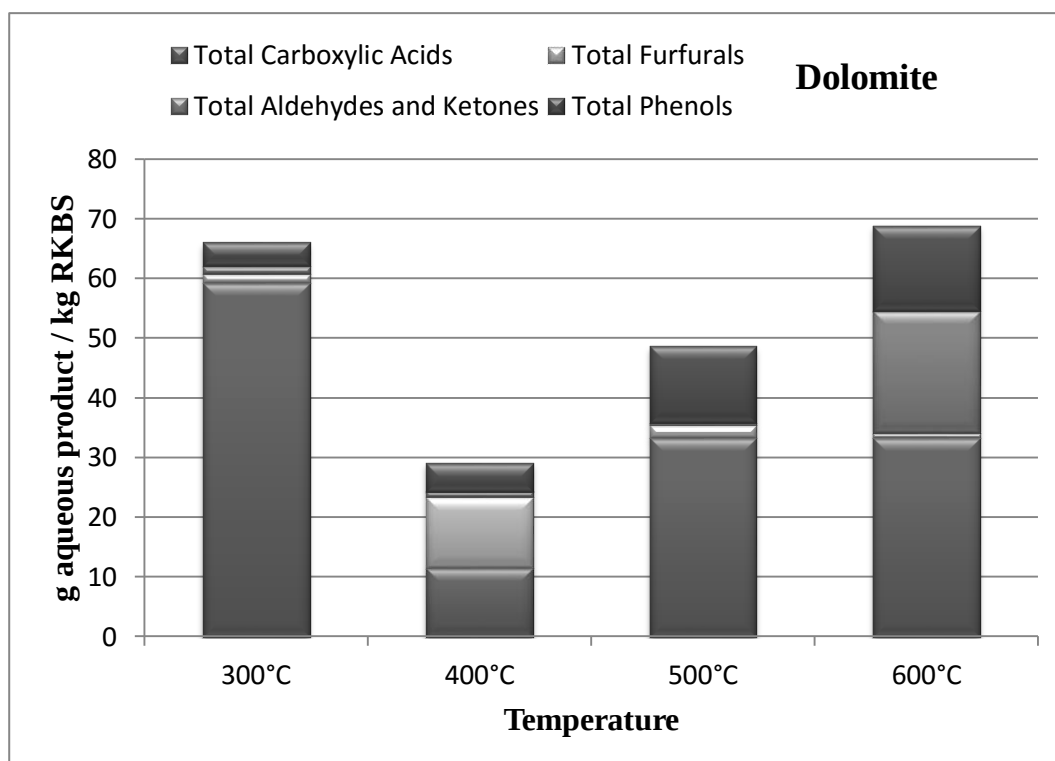


Figure 5.2.2.9 Composition of aqueous product for 4 main group at different temperatures of RKBS with Dolomite.

According to Table 4.2.2.10 and Figure 4.2.2.9, there were total phenols increase and total carboxylic acid decreased with increasing temperature for Dolomite catalyst. Additively, there were aldehydes and ketones declining from 300°C to 500°C whereas there was a sharp rising at 500 to 600°C. Total furfurals increased dramatically between 300 – 400°C, decreased between 400 and 600°C. At 300°C, Total carboxylic acids was the highest yield with 59.26 g/kg RKBS. At 600°C, Glycolic acid and 2-Cyclopenten-1-on shared highest concentration in liquid products with 20.01 g.

Table 5.2.2.11 Variation of liquid product composition of RKBS depends on temperature with Borax in g/kg RKBS.

Borax					
Products		300°C	400°C	500°C	600°C
Total Carboxylic Acids	Glycolic Acid	12.34	13.30	12.44	2.12
	Formic Acid	19.03	31.69	9.24	4.25
	Acetic Acid	4.72	7.67	24.01	9.33
Total Furfurals	5-Methyl furfural	18.87	9.22	40.12	0.73
	1,4 Dioxan	13.79	8.90	9.77	3.70
	Furfural	<0.01	0.01	<0.01	<0.01
Total aldehyde and Ketones	3-Methyl-2-cyclopenten-1-one	0.02	0.01	0.01	<0.01
	2-Cyclopenten-1-on	0.86	0.30	0.10	0.05
	Formaldehyde	0.15	0.12	0.21	0.12
	Acetaldehyde	0.13	0.02	0.05	0.03
	Acetone and Propionaldehyde	0.05	0.13	0.16	<0.01
Total Phenols	Phenol	0.02	<0.01	<0.01	<0.01
	m- and p-Cresol	0.06	0.01	0.00	0.11
	o-Cresol	0.17	0.04	0.12	<0.01
	Resorcinol	0.17	0.16	0.05	0.01
	Catechol	1.30	0.22	0.01	0.28
	3-Methoxycatechol	0.19	0.08	0.28	13.23
	Metoxybenzene and 4-methoxyphenol	3.30	2.55	1.92	0.37
	2-6 Dimethoxy phenol	0.18	0.10	0.37	0.10
	2-Methoxy phenol and 3-methoxy phenol	0.15	0.04	0.10	0.02
	4-Methyl guaiacol	0.44	0.19	0.02	0.21
	3,4 Dimethyl phenol	0.16	0.56	0.21	0.12
	4-Vinyl guaiacol	<0.01	0.02	0.12	0.02
	3,5 Dimethyl phenol	<0.01	0.17	0.02	0.05

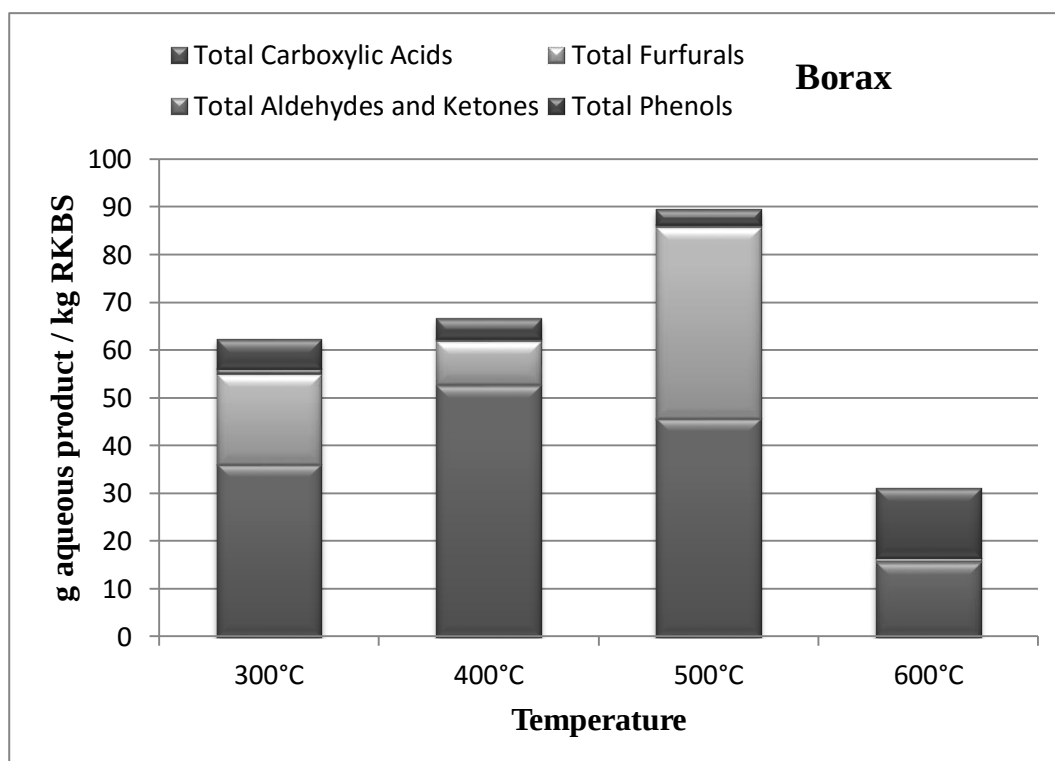


Figure 5.2.2.10 Composition of aqueous product for 4 main group at different temperatures of RKBS with Borax.

Variation of peapod liquid product composition and results of total carboxylic acid, total furfurals total aldehydes and ketones and total phenols with Borax is examined in Table 4.2.2.11 and Figure 4.2.2.10, respectively. Total aldehydes-ketones decreased moderately with increasing temperature. Total carboxylic acids increased at temperatures 300 – 400°C, whereas it tended to decrease between 400 and 600°C. Total phenols declined between 300 – 500°C, increased dramatically between 500 and 600°C. Total furfurals decreased between 300 – 400°C, increased between 400 and 500°C, above 500°C it went up again. At 300°C, Total carboxylic acids was the highest yield with 6.09 g/kg RKBS. 3-Methoxycatrcol had highest concentration in liquid products, with 13.23 g. for 600°C.

Table 5.2.2.12 Variation of liquid product composition of RKBS depends on temperature with KOH in g/kg RKBS.

KOH					
Products		300°C	400°C	500°C	600°C
Total Carboxylic Acids	Glycolic Acid	31.12	4.30	2.32	9.45
	Formic Acid	22.68	16.33	20.00	11.23
	Acetic Acid	5.00	20.86	4.36	12.73
Total Furfurals	5-Methyl furfural	29.19	12.77	0.70	6.42
	1,4 Dioxan	2.84	7.00	3.53	0.84
	Furfural	0.09	<0.01	0.01	0.01
Total aldehyde and Ketones	3-Methyl-2-cyclopenten-1-one	0.04	<0.01	<0.01	<0.01
	2-Cyclopenten-1-on	0.07	0.14	0.20	0.03
	Formaldehyde	0.34	0.29	0.16	0.12
	Acetaldehyde	0.02	<0.01	<0.01	<0.01
	Acetone and Propionaldehyde	0.08	0.19	0.14	0.02
Total Phenols	Phenol	0.02	<0.01	0.01	<0.01
	m- and p-Cresol	0.01	0.01	0.09	0.09
	o-Cresol	0.10	0.14	0.13	9.45
	Resorcinol	0.30	0.10	0.09	<0.01
	Catechol	0.13	0.08	0.04	<0.01
	3-Methoxycatechol	0.20	0.07	0.16	0.07
	Metoxybenzene and 4-methoxyphenol	3.16	0.94	1.66	0.26
	2-6 Dimethoxy phenol	0.36	0.13	0.12	0.86
	2-Methoxy phenol and 3-methoxy phenol	0.32	0.16	0.34	0.00
	4-Methyl guaiacol	0.45	0.14	<0.01	<0.01
	3,4 Dimethyl phenol	0.19	0.48	1.19	0.01
	4-Vinyl guaiacol	<0.01	0.09	0.40	0.01
	3,5 Dimethyl phenol	0.01	0.03	0.06	0.03

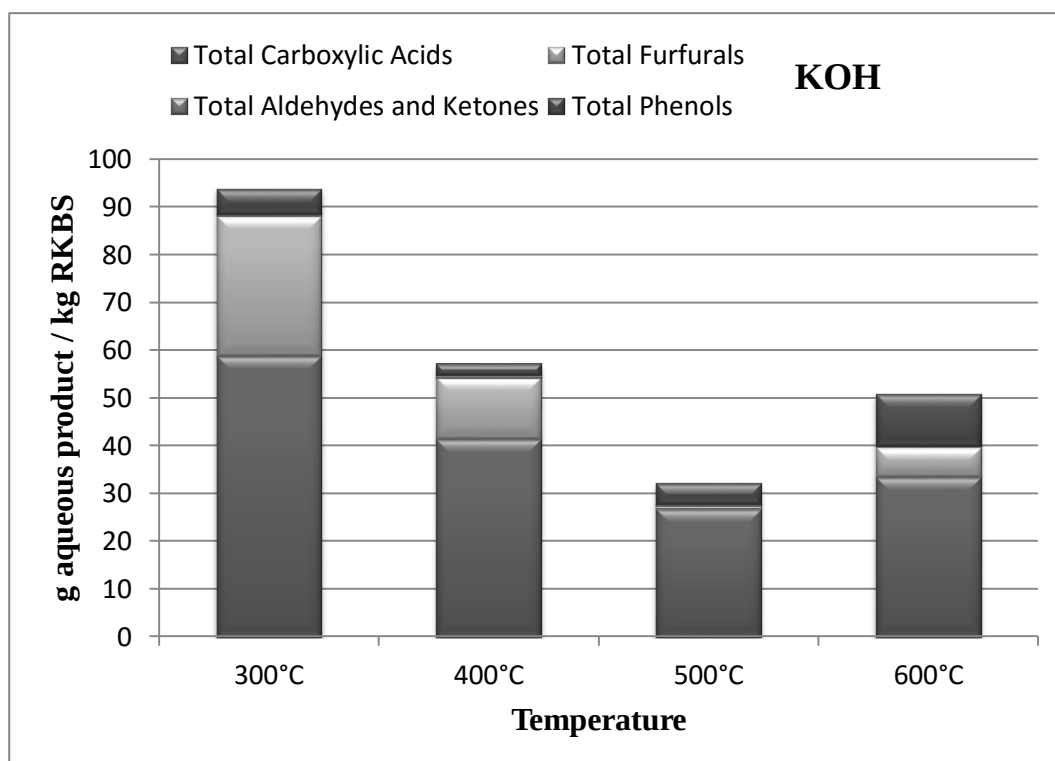


Figure 5.2.2.11 Composition of aqueous product for 4 main group at different temperatures of RKBS with KOH.

Table 4.2.2.12 and Figure 4.2.2.11 gives change of aqueous products for KOH experiments with respect to temperature. Total aldehyde and ketones increased until 400°C and then decreased when temperature increased from 400 to 600°C. Total furfurals and total carboxylic acids dropped strongly from temperature 300 to 500°C and declined dramatically from temperature 500 to 600°C. Total phenols decreased until 400°C and then rose sharply when temperature increased from 400 to 600°C. At 300°C, Total carboxylic acids was the highest yield with 58.80 g/kg RKBS. At 600°C, Acetic acid had highest concentration in liquid products like Trona with 12.73 g.

Table 5.2.2.13 Variation of liquid product composition of RKBS depends on temperature with NaOH in g/kg RKBS.

NaOH					
Products		300°C	400°C	500°C	600°C
Total Carboxylic Acids	Glycolic Acid	40.81	2.47	4.67	15.80
	Formic Acid	2.86	7.74	19.25	23.78
	Acetic Acid	12.49	20.62	5.65	6.70
Total Furfurals	5-Methyl furfural	17.31	40.56	1.07	1.46
	1,4 Dioxan	8.81	6.03	4.07	0.88
	Furfural	0.07	0.00	0.00	0.00
Total aldehyde and Ketones	3-Methyl-2-cyclopenten-1-one	0.05	0.00	0.00	0.00
	2-Cyclopenten-1-on	0.67	0.26	0.07	0.00
	Formaldehyde	0.17	0.28	0.18	0.30
	Acetaldehyde	0.09	0.02	0.00	0.00
	Acetone and Propionaldehyde	0.09	0.19	0.23	0.01
Total Phenols	Phenol	0.01	0.00	0.01	0.00
	m- and p-Cresol	0.01	0.00	0.06	0.10
	o-Cresol	0.01	0.34	0.65	0.18
	Resorcinol	0.18	0.07	0.10	1.26
	Catechol	0.15	0.06	0.02	0.00
	3-Methoxycatechol	0.08	0.10	0.21	2.12
	Metoxybenzene and 4-methoxyphenol	2.09	1.19	1.71	2.46
	2-6 Dimethoxy phenol	0.09	0.16	0.14	2.59
	2-Methoxy phenol and 3-methoxy phenol	0.16	0.23	0.07	0.00
	4-Methyl guaiacol	0.12	0.46	0.04	3.58
	3,4 Dimethyl phenol	0.11	0.55	1.03	4.34
	4-Vinyl guaiacol	0.01	0.04	0.41	4.65
	3,5 Dimethyl phenol	0.01	0.04	0.01	0.00

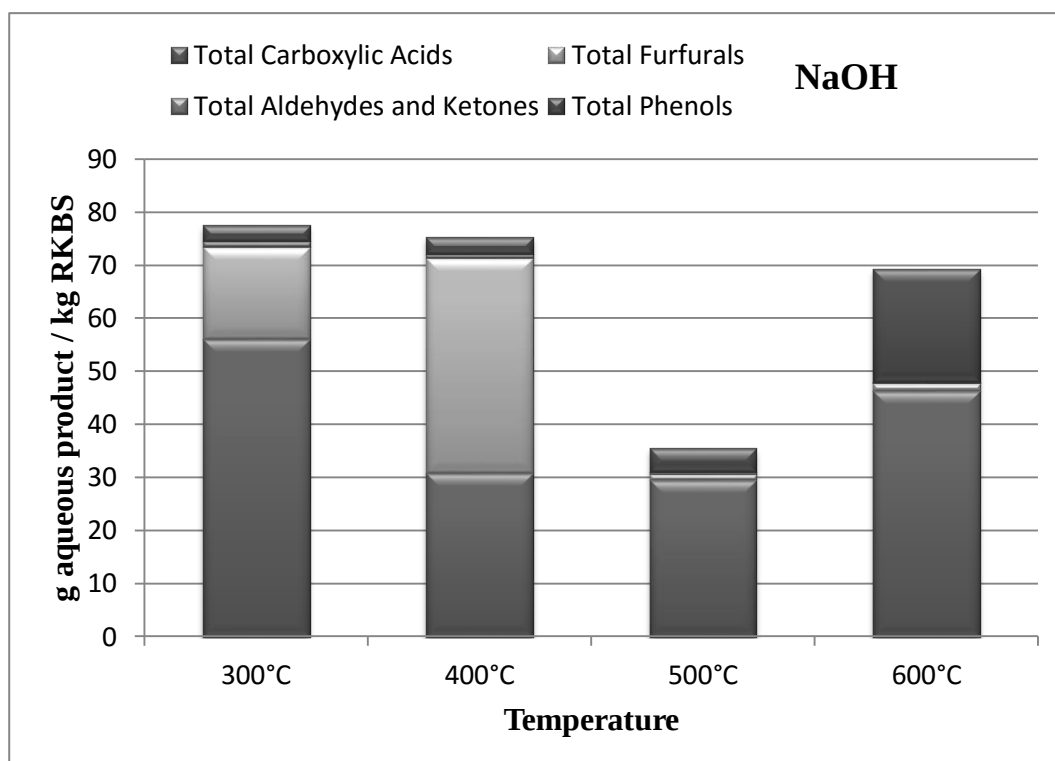


Figure 5.2.2.12 Composition of aqueous product for 4 main group at different temperatures of RKBS with NaOH.

According to Table 4.2.2.13 and Figure 4.2.2.12, there were total aldehydes and ketones decrease with increasing temperature for NaOH catalyst. Total carboxylic acids decreased between 300 – 500°C, increased between 500 and 600°C. Total furfurals rose sharply between 300 – 400°C, declined suddenly between 400 and 500°C, above 500°C it went slightly up again. Total phenols increased continuously with increasing temperature where there was a sharp increment between 500 and 600°C. At 300°C, Total carboxylic acids was the highest yield with 56.16 g/kg RKBS. Formic acid had highest concentration in liquid products just like no catalyst with 23.78 g. for 600°C.

5.3 General Overview of the Results

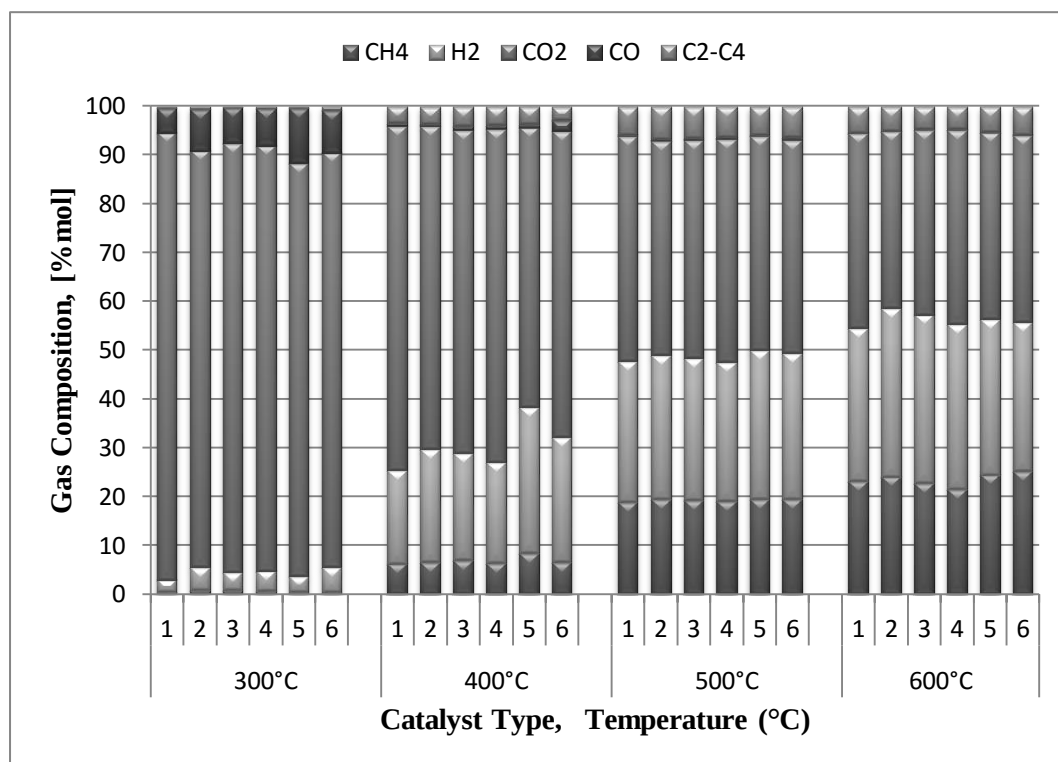


Figure 5.3.1 Variation of gas product composition with temperature and catalyst for SCWG of **peapod** (1: without catalyst, 2: Trona, 3: Dolomite, 4: Borax, 5: KOH, 6: NaOH).

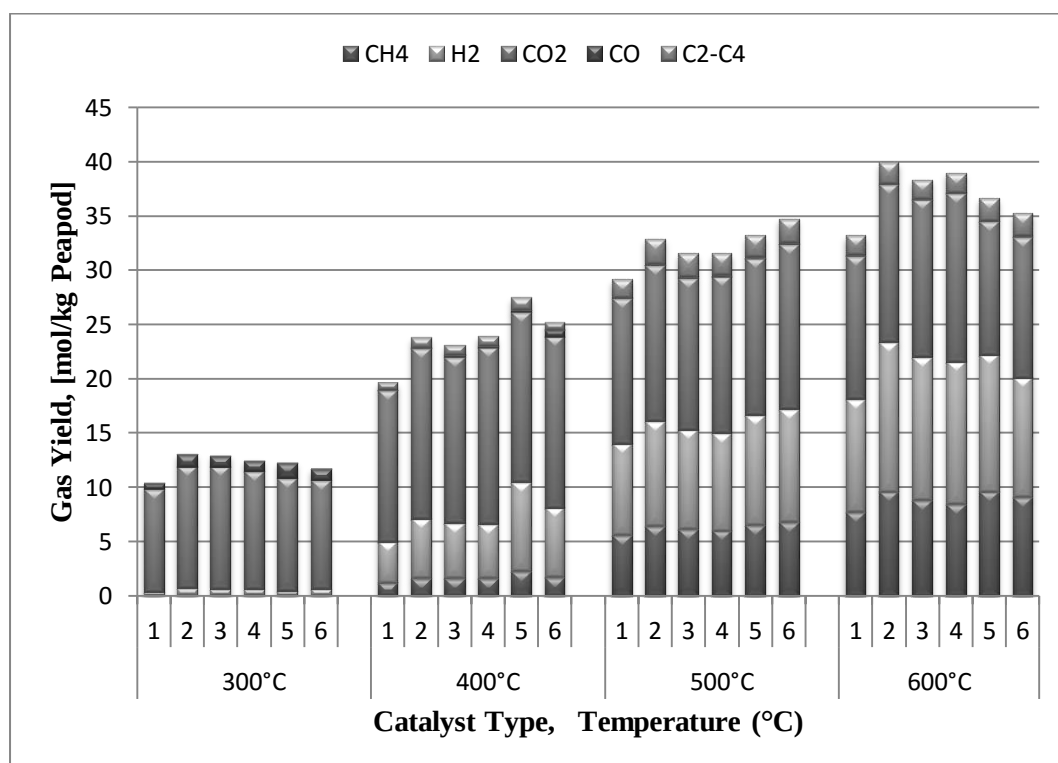


Figure 5.3.2 Variation of gas yield of CH₄, H₂, CO₂, CO, C₂-C₄ with temperature and catalyst for SCWG of **peapod** (1: without catalyst, 2: Trona, 3: Dolomite, 4: Borax, 5: KOH, 6: NaOH).

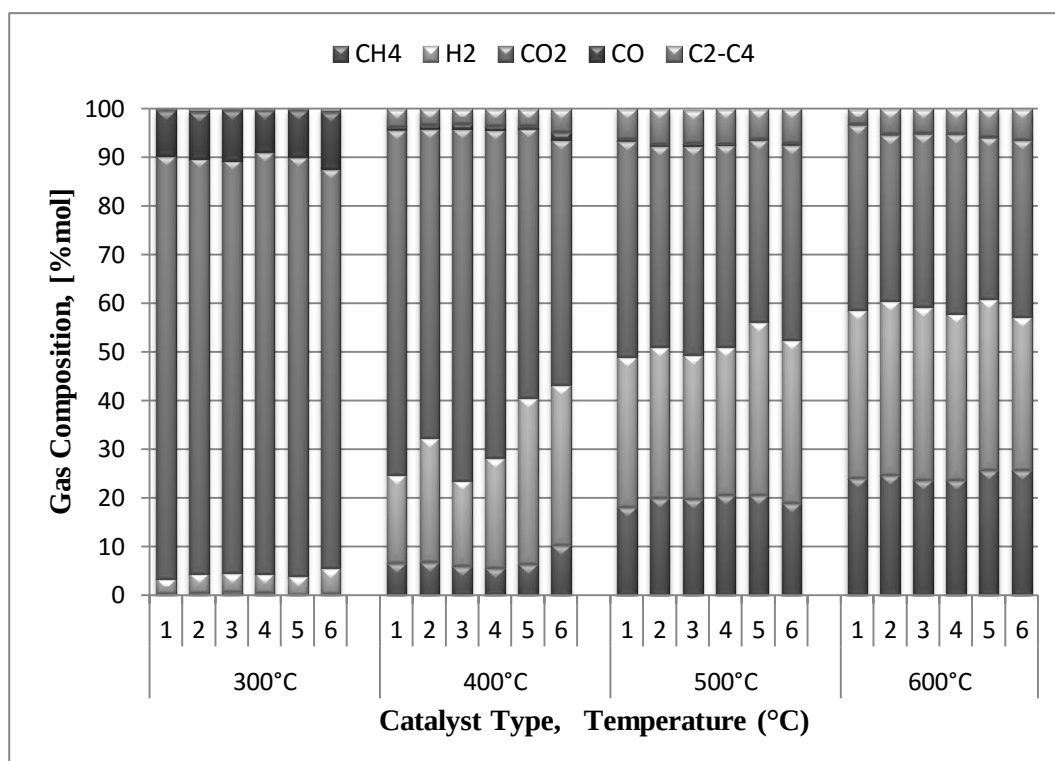


Figure 5.3.3 Variation of gas product composition with temperature and catalyst for SCWG of **Red Kidney Ben Shells** (1: without catalyst, 2: Trona, 3: Dolomite, 4: Borax, 5: KOH, 6: NaOH).

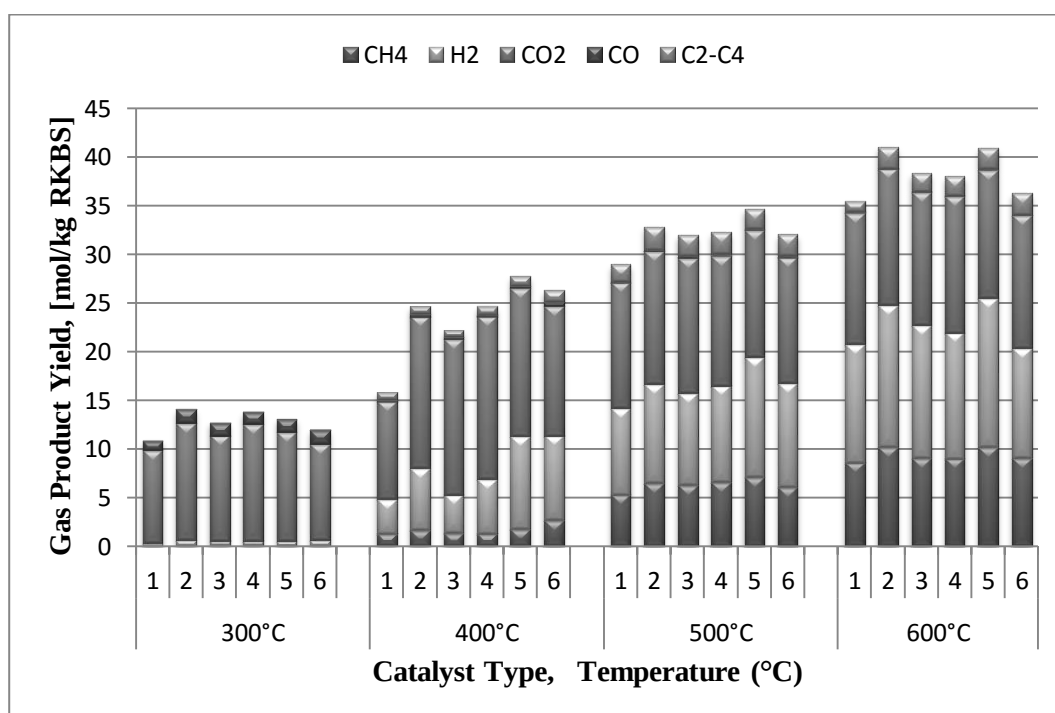


Figure 5.3.4 Variation of gas yield of CH₄, H₂, CO₂, CO, C₂-C₄ with temperature and catalyst for SCWG of **Red Kidney Ben Shells** (1: without catalyst, 2: Trona, 3: Dolomite, 4: Borax, 5: KOH, 6: NaOH).

Figure 5.3.1 – 5.3.4 represents the gaseous compositions in mol % and gas yields in mol/kg Biomass as Peapod and RKBS, respectively. Generally, mol % of CH₄, H₂, and C₂-C₄ increased with increasing temperature, but C₂-C₄ composition was decreasing between 500 and 600°C. Using catalyst raised gas compositions of H₂ and CH₄ as a whole again. For **peapod** experiments, highest mol % of H₂ of were 34.5 % with Trona and Dolomite at 600°C. Maximum composition value of CH₄ was obtained as 25.2 with NaOH at 600°C. For **RKBS**, highest mol % of H₂ were 35.7 % with Trona at 600°C and KOH at 500°C. Maximum composition value of CH₄ was obtained as 25.7 with KOH and NaOH at 600°C. Gas yield of CH₄ and H₂ as mol/kg Biomass increased with increasing temperature. Using catalyst enhanced gas yields of H₂ and CH₄ in general like gas compositions. For **peapod** experiments, highest efficiency of H₂ were 13.8 at 600°C with Trona. Maximum yield of CH₄ was obtained as 9.6 at 600°C with Trona and KOH. For **RKBS** experiments, highest efficiency of H₂ were 15.3 at 600°C with KOH. Maximum yield of CH₄ was obtained as 10.2 with Trona and KOH at 600°C.

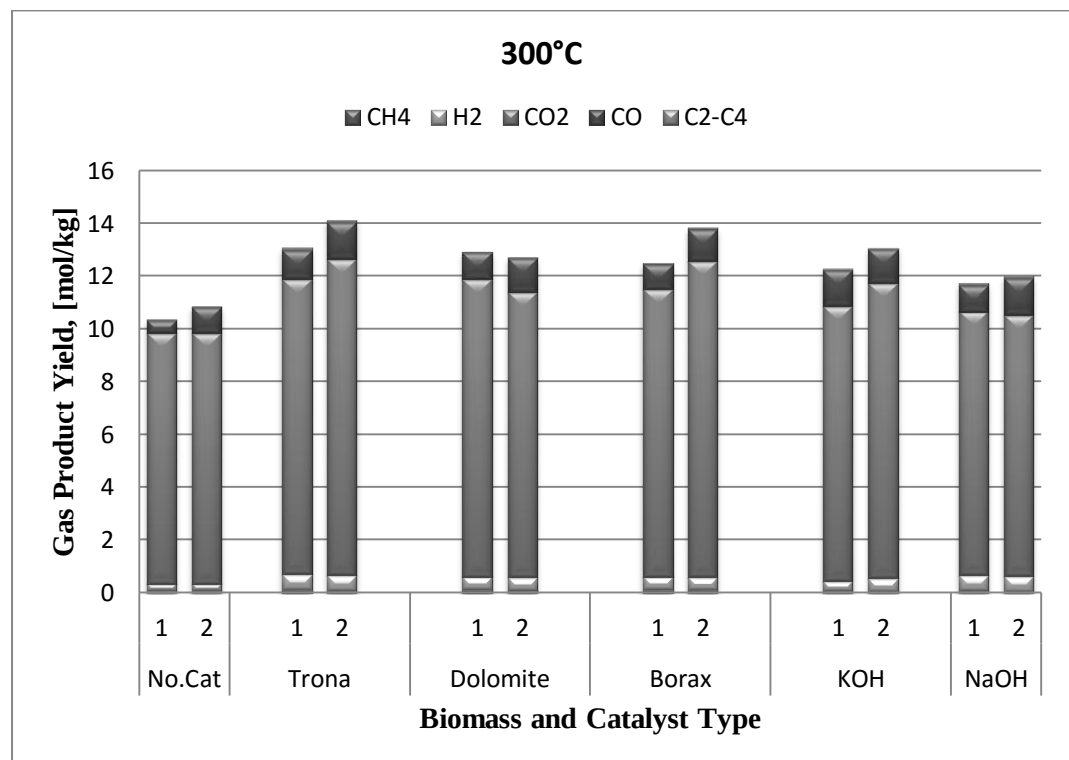


Figure 5.3.5 Variation of gas product composition with temperature and biomass type for SCWG at 300°C (1: Peapod, 2: RKBS).

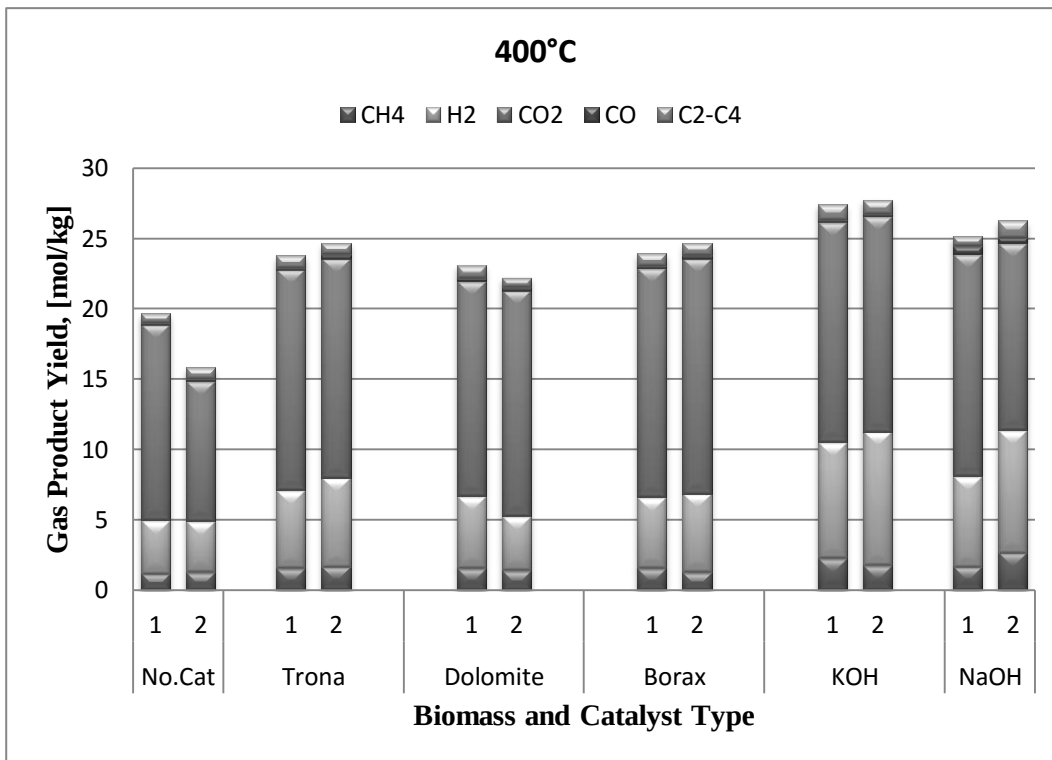


Figure 5.3.6 Variation of gas product composition with temperature and biomass type for SCWG at 400°C (1: Peapod, 2: RKBS).

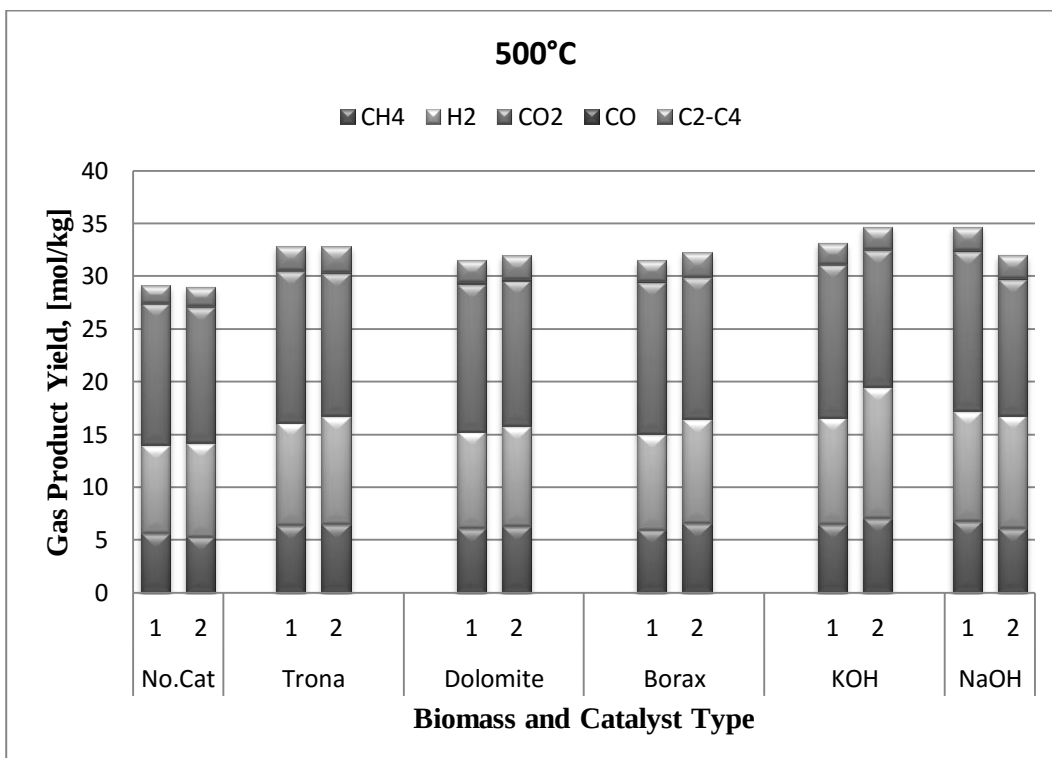


Figure 5.3.7 Variation of gas product composition with temperature and biomass type for SCWG at 500°C (1: Peapod, 2: RKBS).

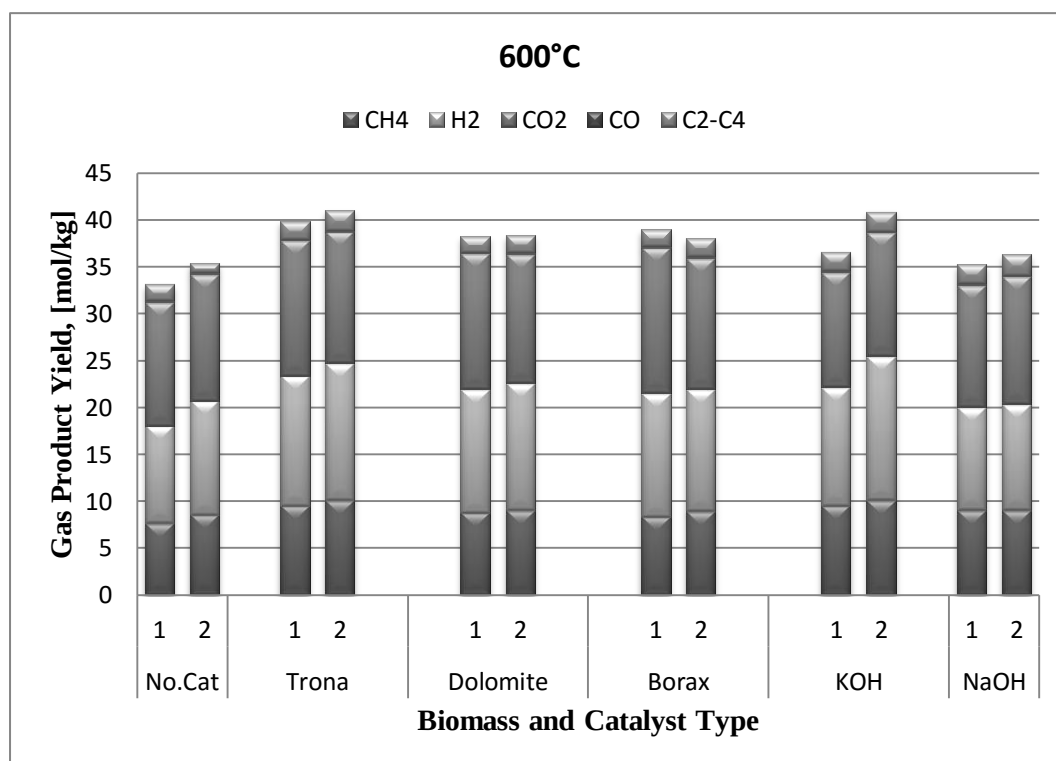


Figure 5.3.8 Variation of gas product composition with temperature and biomass type for SCWG at 600°C (1: Peapod, 2: RKBS).

Figure 5.3.5 – 5.3.8 shows comparison of gas yields of Peapod and RKBS with respect to Biomass and catalyst type. In general, there were approximately same H₂ yield results between two biomass type at low temperatures like 300 – 400°C. Whereas, the H₂ yield of RKBS at higher temperatures at 500 – 600°C was higher than Peapod results. At almost all catalyst type experiments and 600°C, CH₄ yield of RKBS was greater than peapod. On the other hand CO₂ yield of peapod was greater and CO of peapod yield was less than RKBS yields, respectively as a whole.

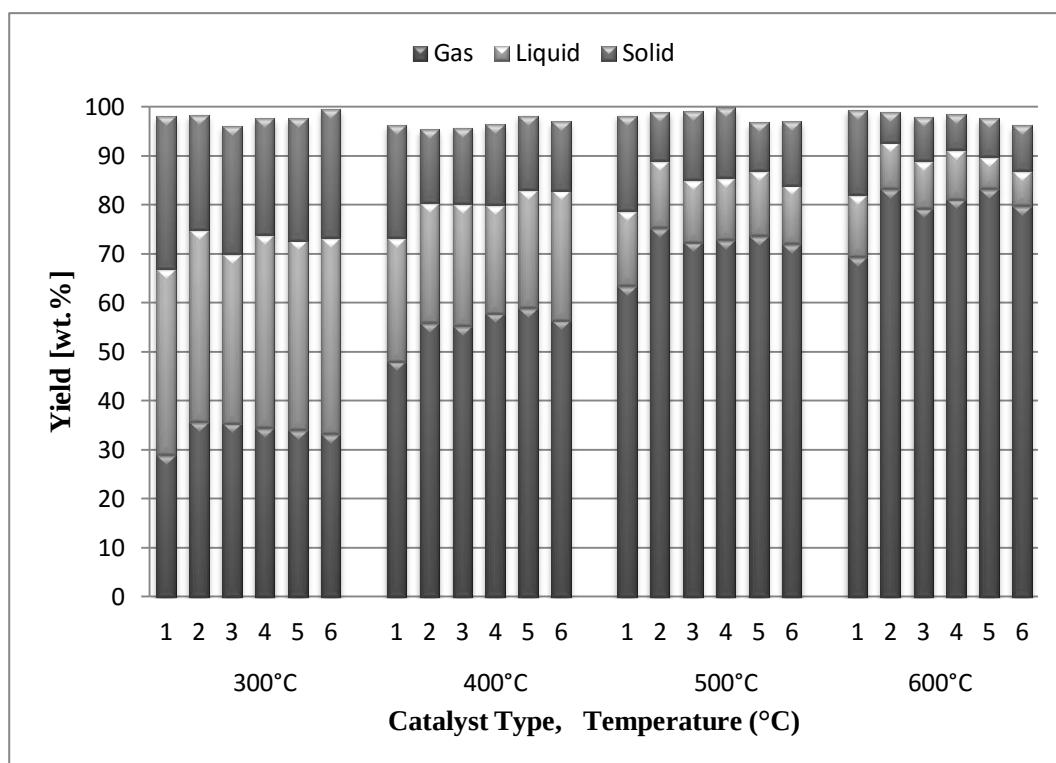


Figure 5.3.9 Variation of gas, liquid and solid yield with temperature and catalyst for SCWG of peapod (1: without catalyst, 2: Trona, 3: Dolomite, 4: Borax, 5: KOH, 6: NaOH).

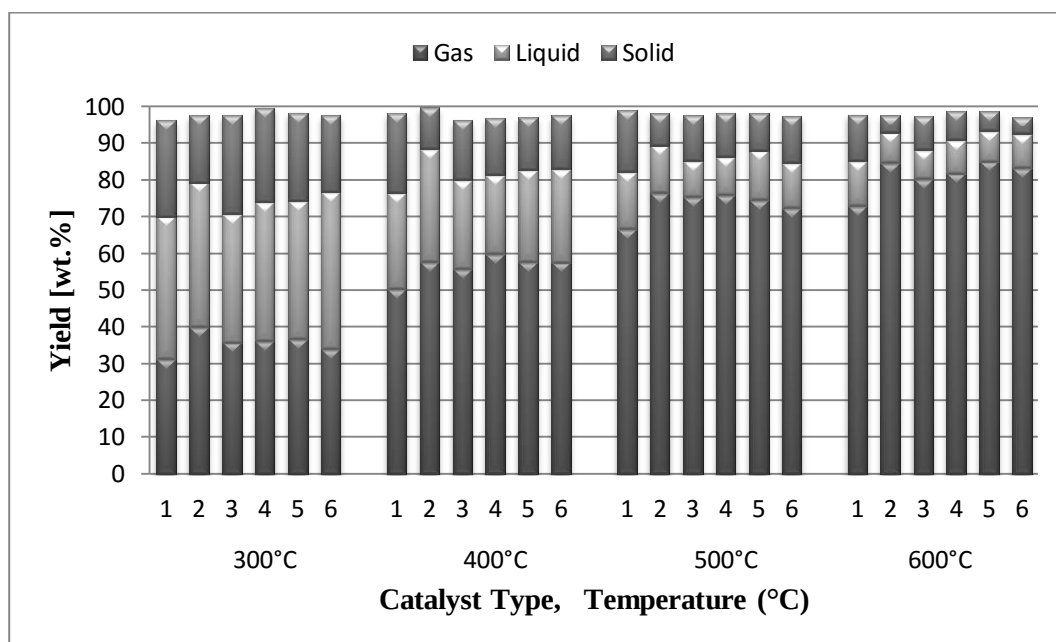


Figure 5.3.10 Variation of gas, liquid and solid yield with temperature and catalyst for SCWG of RKBS (1: without catalyst, 2: Trona, 3: Dolomite, 4: Borax, 5: KOH, 6: NaOH).

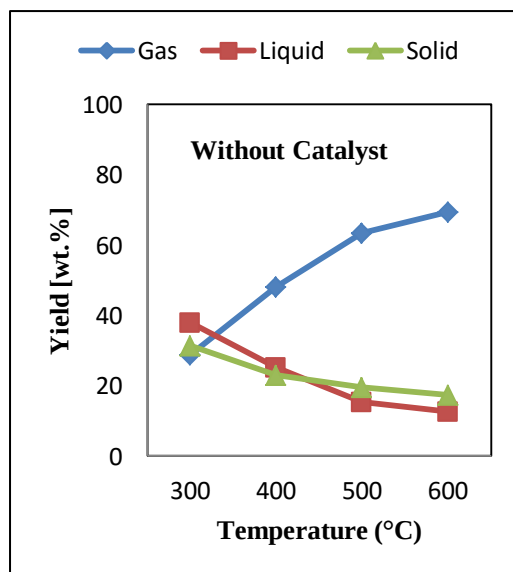


Figure 5.3.11 Variation of gas, liquid and solid yield with temperature for SCWG of **peapod** without catalyst.

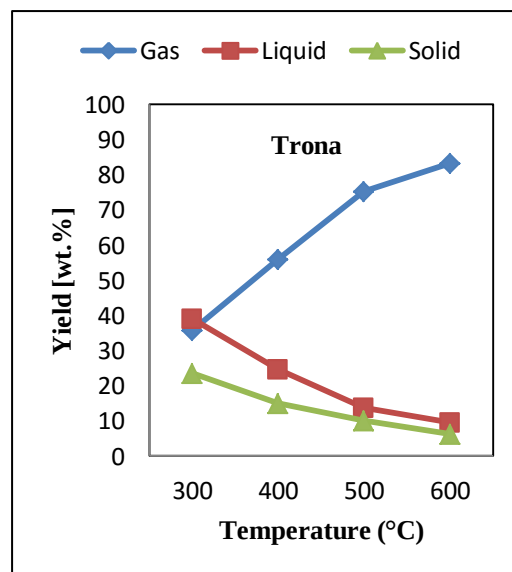


Figure 5.3.12 Variation of gas, liquid and solid yield with temperature for SCWG of **peapod** with Trona.

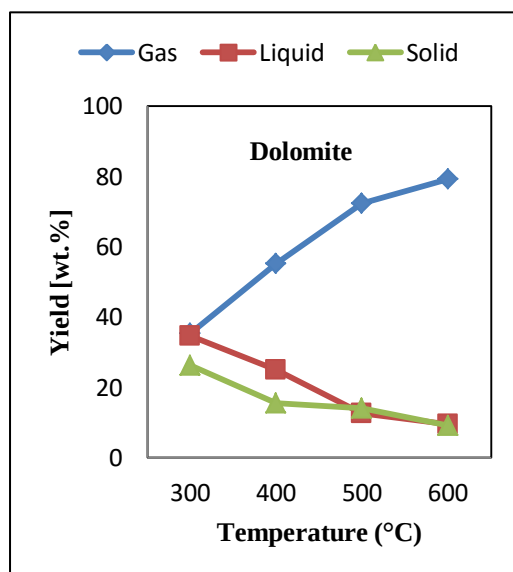


Figure 5.3.13 Variation of gas, liquid and solid yield with temperature for SCWG of **peapod** with Dolomite.

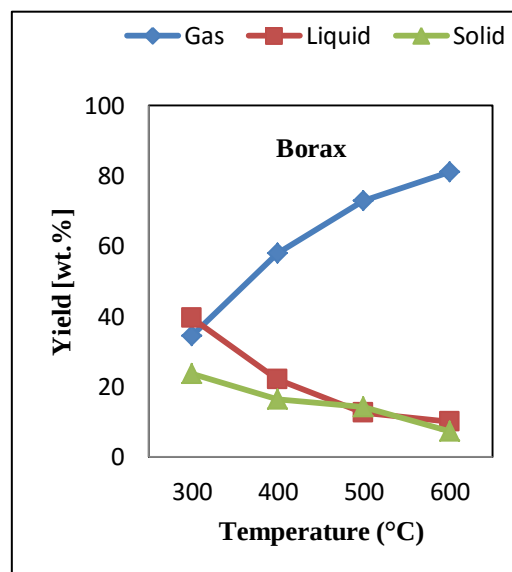


Figure 5.3.14 Variation of gas, liquid and solid yield with temperature for SCWG of **peapod** with Borax.

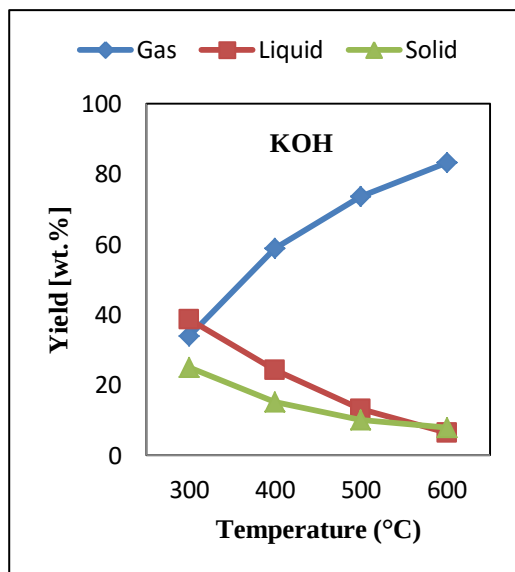


Figure 5.3.15 Variation of gas, liquid and solid yield with temperature for SCWG of **peapod** with KOH.

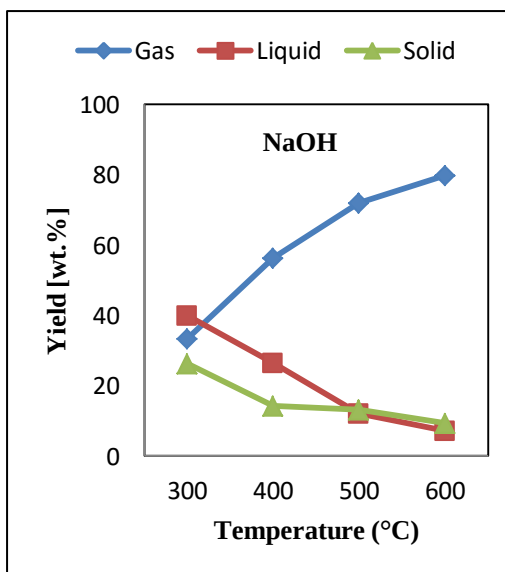


Figure 5.3.16 Variation of gas, liquid and solid yield with temperature for SCWG of **peapod** with NaOH.

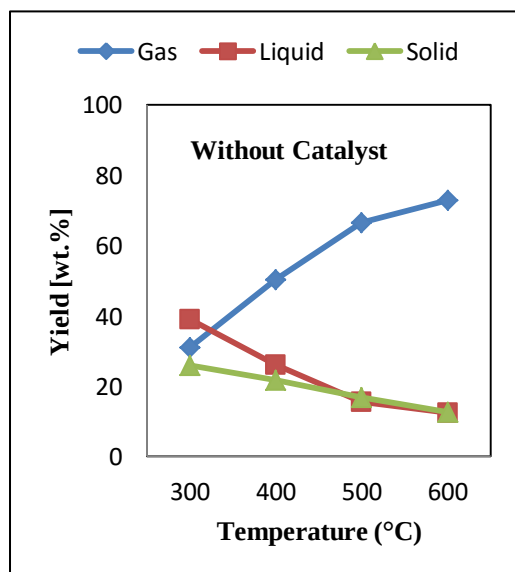


Figure 5.3.17 Variation of gas, liquid and solid yield with temperature for SCWG of **RKBS** without catalyst.

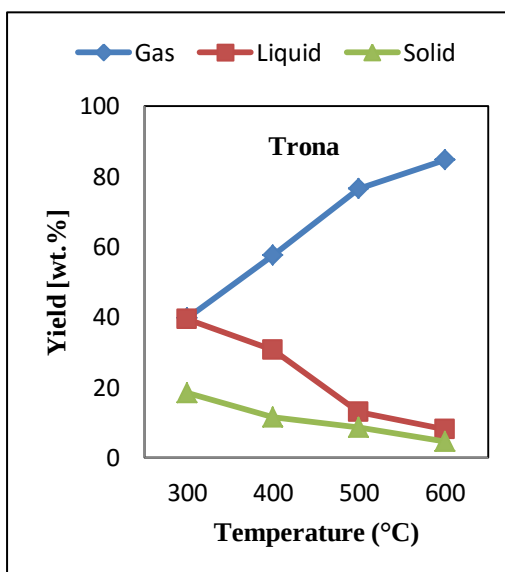


Figure 5.3.18 Variation of gas, liquid and solid yield with temperature for SCWG of **RKBS** with Trona.

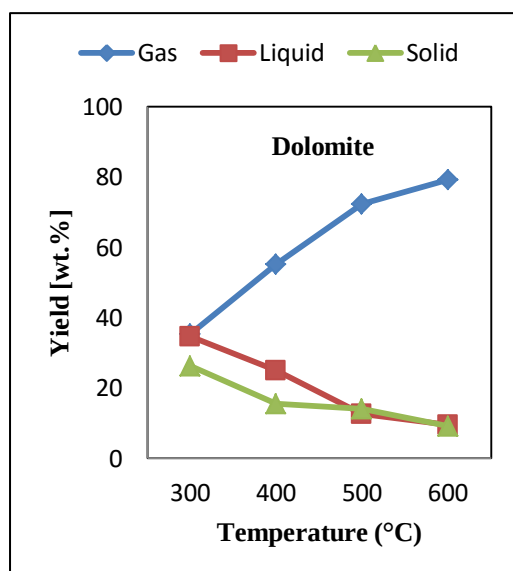


Figure 5.3.19 Variation of gas, liquid and solid yield with temperature for SCWG of **RKBS** with Dolomite.

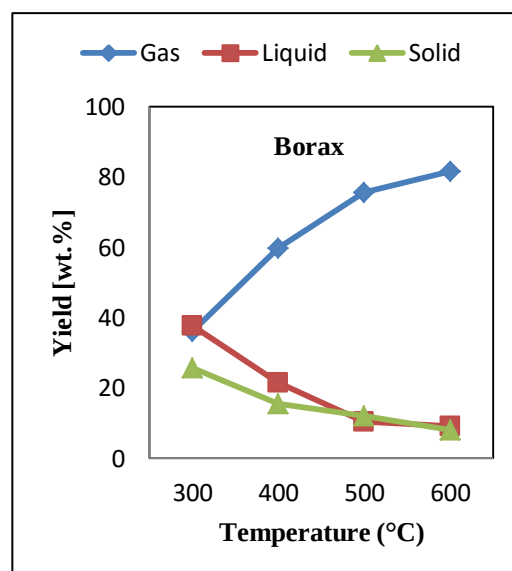


Figure 5.3.20 Variation of gas, liquid and solid yield with temperature for SCWG of **RKBS** with Borax.

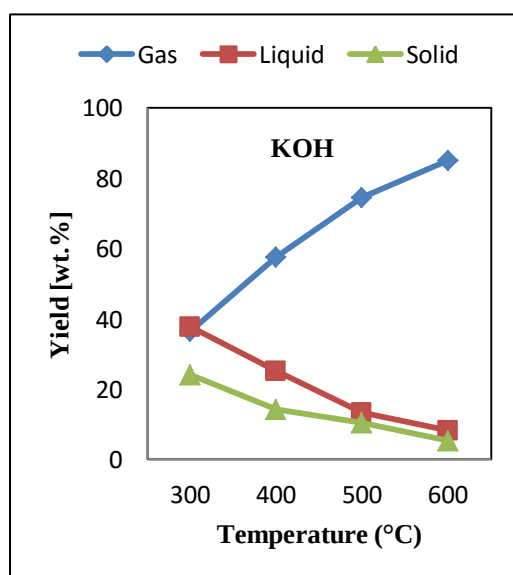


Figure 5.3.21 Variation of gas, liquid and solid yield with temperature for SCWG of **RKBS** with KOH.

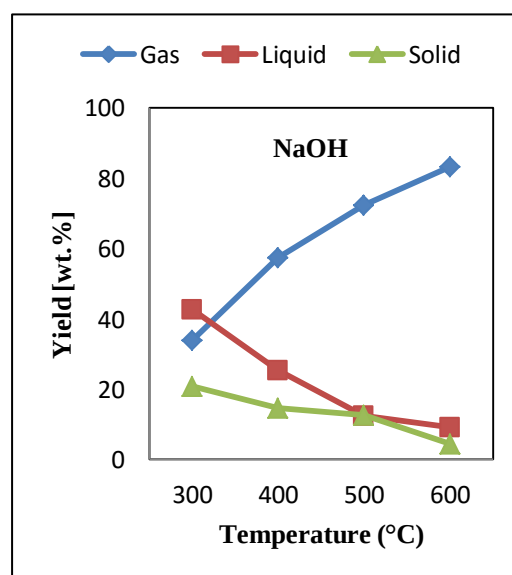


Figure 5.3.22 Variation of gas, liquid and solid yield with temperature for SCWG of **RKBS** with NaOH.

Variations of gas, liquid and solid yields of peapod and RKBS with catalyst and temperature for SCWG were given in Figures 5.3.9 – 5.3.22. As temperature increased, gas product yield increased and liquid and solid product decreased for all experiments. There were gas yield increment in presence of catalyst. **For peapod** experiments, highest gas yield was 83.3 % with KOH at 600°C. Also, KOH had maximum efficiency with 49.3% difference when temperature rising from 300 to 600°C. On the other hand, difference of liquid product yield was 32.9 % was the greatest using NaOH catalyst. Greatest difference of solid product yield was observed with Trona valuing 17.3 %. **For RKBS** experiments, highest gas yield was 85 % for KOH at 600°C. Although, NaOH had maximum efficiency with 49.3 % difference when temperature rising from 300 to 600°C. On the other hand, difference of liquid product yield was 33.5 % was the greatest using NaOH catalyst and the most different value of solid product yield was observed as 18.7 % using KOH with increasing temperature from 300 to 600°C.

6. CONCLUSIONS AND RECOMMENDATIONS

The aim of this experimental study was to investigate the effect of temperature, and catalyst type on supercritical water gasification of red kidney beans and peas wastes. Catalytic and non-catalytic SCWG experiments were carried out in a batch autoclave at four different temperatures (300, 400, 500, 600°C). Trona, Dolomite, Borax, KOH, NaOH were used as catalysts for each biomass type (peapod and RKBS).

Proximate–ultimate analysis and composition of biomass were demonstrated in Table 4.1.1 and 4.1.2, respectively. Experimental results of peapod and RKBS were indicated in Tables 5.1 – 5.12. Gas product compositions and gas yields of peapod and RKBS with and without catalysts were showed in Figures 5.1.1.1 to 5.1.1.12 and Figures 5.2.1.1 to 5.2.1.12, respectively. The amount of TOC in liquid product for each experiments were represented in Tables 5.2.1.1 – 5.2.1.2 and Figures 5.2.1.1 – 5.2.1.2. HPLC results of liquid products with and without catalysts were gave in Tables 5.2.2.2 - 5.2.2.13 and Figures 5.2.2.1 - 5.2.2.12. Finally, general overview of the results for gas, liquid and solid product yields were indicated in Figures 5.3.1 to 5.3.22.

6.1 Conclusions

❖ When the temperature increases,

- mol CH₄ and H₂ / kg biomass increased for whole experiments.
- Amount of CO and CO₂ in gaseous products decreased, but the amount of H₂ and CH₄ increased.
- TOC in liquid product decreased as expected. Because, conversion to gas product increased.
- Total yields of carboxylic acids, furfurals and phenols decreased.
- Total yields of aldehyde and ketones increased first and then decreased because of increasing yields of acetone and propionaldehyde up to 500 °C and nearly vanished at 600 °C.
- Gas product yield increased, liquid and solid product yields decreased.

❖ In the case of catalytic experiments,

- H₂ gas yield increased, CH₄ gas yield increased a small amount.

- Gas product yield increased, liquid and solid yields decreased.
- The highest H₂ yield (mol/kg biomass) at 600°C were obtained in the RKBS experiments with KOH catalyst as 15.3. As salt addition accelerate WGS reaction.
- The highest CH₄ yield (mol/kg biomass) at 600°C were obtained in the RKBS experiments with Trona and KOH catalyst as 10.2.
- Gas yield was at highest level as 85 % in all experiments at 600°C with RKBS and KOH catalyst.
- Liquid yield was at lowest level as 6.5 % in catalytic experiments at 600°C with peapod and KOH catalyst.
- Solid yield was at lowest level as 4.5 % in catalytic experiments at 600°C with RKBS and NaOH catalyst.
- TOC amount of liquid product is effected by catalyst addition. The highest difference (1530ppm) in TOC values between the 300°C – 600°C belonged to experiments with RKBS and NaOH and the lowest one belonged to experiments with peapod and Dolomite.
- Generally, the highest amount of compound group in aqueous products was carboxylic acids for all studied reaction conditions.
- The highest total carboxylic acids yields were obtained at 300 °C with peapod in the presence of Borax.

6.2 Recommendations

- Gas yield is effected from reaction temperature extremely. Gas yield rise and types of organic compounds and their amounts in liquid phase decline at high temperature. Therefore, temperature can be adjusted according to desired products.
- The most efficient catalyst was KOH. Although, natural minerals like Trona, Dolomite and Borax can be useful for supercritical water gasification of biomass. They can be nearly effective as alkali catalysts in SCWG for large quantity gasification.

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RESUME

Doğan Emre YÜKSEL was born in Ankara in 1988. He received her BSc. Degree from Ege University Chemical Engineering Department in 2012. Last year of the BSc. Degree she studied with Prof. Dr. Levent Ballice on the topic of “Sub and Supercritical Water Gasification of a Woody Biomass Fir” in his graduation thesis Project.

After three year of his BSc. He went to Politecnico di Torino (Italy) with ERASMUS Program. He took some courses of BSc. education, there.

He completed his MSc. Thesis which was “Investigation of the Effect of Temperature, Pressure and Catalyst on Evolution of Hydrogen and Methane in Supercritical Water Gasification of Red Kidney Beans and Peas Wastes” under supervisor Prof. Dr. Levent Ballice at Ege University in October, 2015.

APPENDICES

Appendix 1 Calculations of Feed Amount, Gas and Liquid Products

Appendix 1 Calculations of Feed Amount, Gas and Liquid Products

Sample: Peapod, **Temperature:** 300°C, **Catalyst type:** No catalyst

Amount of peapod and organic C fed to the reactor:

1.2 g peapod and 15 ml water:

Humidity of peapod = 10.07 %

Humidity content = $1.2 * 0.1007 = 0.12084$ g

Dry peapod = $1.2 \text{ g} - 0.12084 \text{ g} = 1.07916 \text{ g}$

C content of peapod in feed = 42.30 %

Total organic carbon = $1.07916 * 0.4230 = 0.4565 \text{ g C} = 456.48 \text{ mgC}$

Calculations of gas products:

➤ Gas product composition, mole:

From ideal gas law : $n = \frac{P*V}{R*T}$

$T_{\text{ambient}} = 293 \text{ K}$, $V_{\text{gas product}} = 0.3 \text{ L}$

$P = 1 \text{ atm}$, $R = 0.082 \text{ L.atm/mol.K}$

$n_{\text{total}} = 0.0125 \text{ mol}$

Moles of H_2 = mole % of H_2 * $n_{\text{total}}/100$ (Data from the GC analysis results)

$$= \frac{2.6 * 0.0125}{100} = 3.25 * 10^{-4} \text{ mol H}_2$$

For calculating this value N_2 amounts in product gas was considered.

Other gas product moles were calculated in the same way.

➤ Calculation of H_2 gas mol per kg peapod:

$$\text{Amount of H}_2 \text{ mol/kg peapod} = \frac{\text{Amount of H}_2 \text{ mol}}{\text{Amount of peapod feed to reactor}}$$

$$= \frac{3.25 \times 10^{-4}}{1.07916 \times 10^{-3}} = 0.3 \text{ mol H}_2 / \text{kg peapod}$$

All compounds (except N₂) in gas phase were determined by similar calculations.

➤ Calculation of H₂ gas g / kg peapod:

$$\text{Amount of H}_2 \text{ g/kg peapod} = \frac{\text{Amount of H}_2 \text{ mol} * \text{MW}_{\text{H}_2}}{\text{Amount of peapod feed to reactor}}$$

$$= \frac{3.25 \times 10^{-4} * 2}{1.07916 \times 10^{-3}} = 0.6 \text{ g H}_2 / \text{kg peapod}$$

All compounds (except N₂) in gas phase were determined by similar calculations.

Total gas amount per peapod = 434.4 g/kg peapod

➤ Calculation of gas yield:

$$\text{Gas yield} = \frac{\text{Total amount of C in gas product}}{\text{Amount of organic C fed to reactor}} * 100$$

Amount of C in CH₄ (mg) = (Amount of C in CH₄, mmol) × (Number of C in CH₄ molecule) × MW_{CH₄}

$$0.0125 * 0.004 * 1 * 16 = 8 * 10^{-4} \text{ g} = 0.8 \text{ mg}$$

All compounds (except N₂ and H₂) in gas phase were determined by similar calculations.

Total amount of C in gas product = 131.93 mg

$$\text{Gas yield} = \frac{131.93}{456.48} * 100 = 28.9 \%$$

➤ Calculation of liquid yield:

$$\text{Carbon content of liquid product, mg} = \frac{\text{TOC of liquid product, ppm} * \text{V liquid, mL}}{1000 \text{ mL.L}^{-1}}$$

$$= \frac{1730 * 100}{1000} = 173 \text{ mg}$$

$$\text{Liquid yield} = \frac{\text{Total amount of C in liquid product}}{\text{Amount of organic C fed to reactor}} * 100$$

$$= \frac{173}{456.48} * 100 = 37.9 \%$$

➤ Calculation of solid yield:

$$m_{\text{coke}} = 0.2294 \text{ g}$$

From SSM result, TOC of coke = 62.28 %

Carbon content of solid product,mg = $0.2294 * 0.6228 = 0.1429 \text{ g Carbon}$

$$\text{Solid yield} = \frac{\text{Total amount of C in solid product}}{\text{Amount of organic C fed to reactor}} * 100$$

$$= \frac{0.1429}{0.45648} * 100 = 31.3 \%$$