ÇUKUROVA UNIVERSITY
INSTITUTE OF NATURAL AND APPLIED SCIENCES

M.Sc. THESIS

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UPGRADING FUEL CHARACTERISTIC OF POULTRY SLUDGE VIA WET TORREFACTION

DEPARTMENT OF MECHANICAL ENGINEERING

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ABSTRACT

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The main barriers to the use of biomass as an energy source are high humidity, ash, and oxygen content which can be eliminated by wet torrefaction (WT). In this study, dewatered poultry sludge (DPS), as being complex biomass to dispose of, was subjected to WT by considering the reaction temperature, time, and feed concentration as the independent process parameters. The parameter range is determined using response surface methodology and the experiments were carried out in a laboratory-scale batch reactor. The optimum conditions for both maximum solid yield (SY) and calorific value (CV) were evaluated for the reaction temperature, time, and feed concentration of 268°C, 47 min, 50wt%, respectively. According to the results, the feed concentration was the most influential parameter on calorific value and solid yield, whereas the reaction time has the lowest effect. In addition to their individual effects, the interactive effects of process parameters on CV and SY were also analyzed by two and three-dimensional contour plots. Besides, the proximate analysis revealed that the fixed carbon was observed to be increased while the amount of ash and volatile matter in the torrefied DPS (TDPS) decreased under optimum conditions. Through the ultimate analysis, a remarkable reduction in the atomic ratio of oxygen to carbon was reported. According to the results it is concluded that the WT significantly enhances and converts raw poultry sludge to a more efficient solid fuel.

Keywords: biomass, dewatered poultry sludge, wet torrefaction, hydrochar, proximate analysis, elemental analysis.

ÖZ

YÜKSEK LİSANS TEZİ

ISLAK TOREFAKSİYON YÖNTEMİ İLE KANATLI ÇAMURUNUN YAKIT ÖZELLİĞİNİ GELİŞTİRME

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Biyokütlenin bir enerji kaynağı olarak kullanılmasının önündeki ana engeller, ıslak torrefaksiyon (WT) ile ortadan kaldırılabilen yüksek nem, kül ve oksijen içeriğidir. Bu çalışmada, bertaraf edilmesi zor, karmaşık bir biyokütle olan susuzlaştırılmış kanatlı çamuru (DPS), bağımsız proses parametreleri olarak reaksiyon sıcaklığı, süresi ve besleme konsantrasyonu dikkate alınarak WT işlemine tabi tutulmuştur. Parametreler yanıt yüzey metodu kullanılarak tasarlanmış olup, deneyler laboratuvar ölçekli kesikli reaktörde gerçekleştirilmiştir. En yüksek katı verimi (SY) ve ısıl değeri (CV) hedefleyen optimum koşullar, 268°C reaksiyon sıcaklığı, 47 dakika reaksiyon süresi ve ağırlıkça 50% besleme konsantrasyonu olarak değerlendirilmiştir. Sonuçlara göre, besleme konsantrasyonu ısıl değer ve katı verimi üzerinde en etkili parametre iken, reaksiyon süresi en düşük etkiye sahiptir. Bireysel etkilerine ek olarak, proses parametrelerinin SY ve CV üzerindeki interaktif etkileri de üç ve iki boyutlu kontur dağılımları ile analiz edilmiştir. Ayrıca, optimum koşullar altında torrefe edilmiş DPS'deki (TDPS) kül ve uçucu madde miktarının azaldığı, sabit karbonun arttığı yaklaşık analiz vasıtası ile ortaya çıkarılmıştır. Nihai analiz yoluyla, oksijen-karbon atomik oranında dikkate değer bir azalma rapor edilmiştir. Bu sonuçlar ile, WT işleminin biyokütleyi önemli ölçüde geliştirdiği ve daha verimli bir katı yakıta dönüştürdüğü sonuçlarına varılmıştır.

Anahtar Kelimeler: biyokütle, susuzlaştırılmış kanatlı çamuru, ıslak torrefaksiyon, hidroçar, yaklaşık analiz, nihai analiz.

EXTENDED ABSTRACT

The use of fossil fuels as an energy source brings many environmental problems like global warming and pollution. The search for alternative fuels has directed scientists to various renewable energy sources such as solar energy, geothermal energy, wind energy, and bioenergy. Compared to fossil fuels, biomass is a promising energy source as it can be found more easily and in abundance in almost every region of the world and different varieties. However, biomass cannot be used directly as an efficient fuel due to its high moisture, ash, and oxygen levels. While the moisture and oxygen content reduce the calorific value, ash content brings wide variation in chemical composition.

Animal slaughterhouse wastes, which play an important role in waste biomass production, were chosen as raw materials in this study. In the poultry slaughtering industry, a large amount of water is used for meat production and a large amount of wastewater is generated as a result of production. The wastewater is treated with a dewatering process, which results in a physicochemical sludge that contains a high amount of animal protein, fat and pathogenic bacteria. This sludge in a poultry slaughterhouse called dewatered poultry sludge (DPS), which is difficult to dispose of, is a substance that has the aforementioned biomass disadvantages but a high calorific value potential (26586.66 J/g). Another attractive feature of DPS is its high amount of feedstock with continuous production. The feedstock rate of DPS can approach up to 80 tons per day. The wet torrefaction (WT) process, by avoiding the biomass drying process, is considered quite efficient in eliminating the negative side of the fuel properties of biomass. The WT process is usually carried out in the temperature range of 180-280 °C because it takes advantage of the properties of subcritical water. Subcritical water has unique properties suitable for biomass conversion, for example, both density and dielectric constant decrease with temperature while the ionic product increases. Besides, during the hydrothermal torrefaction of biomass, water acts as both the reaction

medium and the reactant, so the feedstock does not have to be dried. Another feature of subcritical water media is the ability to wash out inorganic parts of biomass, hence the amount of ash in torrefied biomass is reduced. During the literature search, biomass conversion studies related to poultry sludge can be found. However, the current study aims to bring a novelty to the literature by applying WT to DPS using Response Surface Methodology (RSM) considering 3 different independent parameters. The main goal of the study is to obtain the highest possible calorific value together with solid yield by optimizing the independent process parameters with the help of RSM. In this manner, the effects of WT on fuel characteristics of DPS under different experimental conditions were investigated experimentally. The effects of independent process parameters on the fuel properties of DPS were elaborated utilizing proximate, ultimate, and calorific value analysis on the product.

The current study was started with the supply of DPS from a slaughterhouse, then samples were dried in a conventional oven in order to reduce the moisture content to zero. The drying process was followed by characterization of raw DPS with proximate, ultimate, and energy content analyses according to ASTM standards. For the next step, experiments were designed to carry out the WT process. The RSM was used to design the experiment and optimize experimental conditions for maximum responses. Reaction temperature (°C), reaction time (min), and feed concentration (wt%) were determined as independent process parameters. The responses were termed as the calorific value and solid yield. The number of experiment runs and level of independent process parameters was adjusted by Box-Behnken Design. Sixteen different experiments were carried out in a laboratory-scale batch reactor made of 316 L steel, including 15 design experiments and 1 optimization experiment. Then torrefied DPS was collected for the characterization process. The WT was initiated by loading the DPS with distilled water into the reactor at a predetermined concentration of (10: 30: 50wt%). The rotation of stirring was kept constant at a rate of 100 rpm during mixing. The required inert reaction atmosphere was satisfied by introducing nitrogen at 1 bar into the sealed reactor until air was completely discharged. The pressure was kept constant within the range of sub-critical pressures auto-generated by heat supply. The reactor was kept under a predetermined reaction time interval of (20: 40: 60) min when the reaction temperatures approaches to the desired levels of (180: 230: 260) °C. Then, the reactor was submerged into an ice bath for cooling until the temperature dropped to room temperature. After the cooling process, the products were collected from the reactor. Torrefied DPS and liquid products were separated from each other with the help of a filter paper having 10μm pore size. Torrefied DPS is then subjected to a drying process to eliminate possible reactions during storage that lead to inaccurate results in oncoming analysis. To provide high reliability for results and predict the responses, variance analysis (ANOVA) was performed. Lastly, independent and interactive effects of process parameters were investigated.

Regarding the WT process results, the parameters that have the most prominent effect on the calorific value and solid yield were the feed concentration, followed by the reaction temperature. Therefore, the least effective parameter on responses was determined as reaction time. Since alkali metals act as catalysts during the reaction, the dominant effect of the feed concentration can be explained by the amount of alkali metal in the biomass. The reason why the effect of reaction temperature on the responses is greater than that of the reaction time can be determined with the help of the first-order rate law for a thermal decomposition reaction and the Arrhenius equation. The effect of the process parameters on the responses and the interactive effects between each other has been revealed by two and three-dimensional contour plots. Since it was impossible to represent all three parameters' effect on responses by either a single contour or three-dimensional plot, one of the parameters was maintained at the optimum level with varying two parameters. Besides, the highest calorific value (28867,0 J/g) with 83.31wt% solid yield was obtained at 280 °C, 50wt%, and for 60min, whereas the optimum condition for maximum CV and SY was evaluated at 268°C, 50wt%, and for 47 min. According to variance analysis results, the p-values of the model for responses were found to be less than 0.05 which is within the confidence level of analysis. Thus, models were considered to be statistically significant. On the other hand, the p-values of the lack-of-fit for responses were higher than 0.05; hence the data matched well with the models. Furthermore, the adjusted correlation coefficients of models for CV and SY were found to be 95.05%, 97.02%, respectively. Besides, correlation coefficients are found to be adequate for high accuracy in models.

Considering the proximate analysis results, fixed carbon was found to be increased from 7.41 %wt to 11.7 %wt and the volatile matter was slightly decreased from 67.5 wt% to 66.1 wt%. Furthermore, the amount of ash in the wet torrefied DPS is decreased from 25.09 wt% to 22.18 wt%. According to the elemental analysis, a reduction in the atomic ratio of O/C to 0.158 was reported as a reason for carboxylation reactions.

In conclusion, it was reported in this study that all parameters were found to enhance CV while reaction temperature and time have detrimental effects on the SY by the applied method. According to the analyses of data, ash, O/C, and total solid matter were decreased by 11.59%, 6.51%, 14.80 %, respectively. However, CV was increased by 7.75 % under optimum conditions. Considering these results, it was revealed that fuel properties of torrefied DPS were upgraded and became a more efficient solid fuel. Moreover, the increase in carbon ratio, the decrease in oxygen content, and the amount of ash have transformed the torrefied DPS into a coal-like structure. It is believed that this study may lead to a more detailed examination of the effect of WT on various biomasses and wider application areas of it for future studies.

GENİŞLETİLMİŞ ÖZET

Fosil yakıtların enerji kaynağı olarak kullanılması, küresel ısınma ve kirlilik gibi birçok çevre sorununu beraberinde getirmektedir. Alternatif yakıt arayışları, bilim insanlarını güneş enerjisi, jeotermal enerji, rüzgar enerjisi, biyoenerji gibi çeşitli yenilenebilir enerji kaynaklarına yöneltmiştir. Biyokütle, fosil yakıtlara kıyasla dünyanın hemen her bölgesinde ve farklı çeşitlerde daha kolay ve bol miktarda bulunabilmesi nedeniyle umut vadeden bir enerji kaynağıdır. Ancak yüksek nem, kül ve oksijen seviyeleri nedeniyle doğrudan verimli bir yakıt olarak kullanılamamaktadır. Nem ve oksijen içeriği ısıl değeri düşürürken, kül içeriği kimyasal bileşimde geniş bir çeşitlilik getirir.

Bu çalışmada hammadde olarak atık biyokütle üretiminde önemli rol oynayan kesimhane atıkları seçilmiştir. Kanatlı kesim endüstrisinde et üretimi için büyük oranda su kullanılmakta ve üretim sonucunda önemli miktarda atık su oluşmaktadır. Atık su, yüksek miktarda hayvansal protein, yağ ve patojenik bakteri içeren fizikokimyasal bir çamur oluşturan susuzlaştırma işlemi ile arıtılır. Susuzlaştırılmış kanatlı çamuru (DPS) olarak adlandırılan ve bertaraf edilmesi zor olan kanatlı kesimhanelerindeki bu çamur, daha önce belirtilen biyokütle dezavantajlarına sahip ancak yüksek ısıl değer potansiyeli (26586.66 J/g) olan bir maddedir. DPS'nin bir diğer çekici özelliği de sürekli üretimi ile yüksek miktarda stoğu olmasıdır. DPS'nin stoğu günde 80 tona kadar ulaşabilir. Biyokütle kurutma işleminden kaçınarak, ıslak torrefaksiyon (WT) işleminin, biyokütlenin yakıt özelliklerinin olumsuz taraflarını ortadan kaldırmada oldukça verimli olduğu düşünülmektedir. WT işlemi, subkritik suyun özelliklerinden yararlandığı için genellikle 180-280 °C sıcaklık aralığında gerçekleştirilir. Subkritik su, biyokütle dönüşümü için uygun benzersiz özelliklere sahiptir; örneğin iyonik ürün artarken hem yoğunluk hem de dielektrik sabiti artan sıcaklıkla azalır. Ayrıca, biyokütlenin ıslak torrefaksiyonu sırasında su, hem reaksiyon ortamı hem de reaktan olarak hareket eder, bu nedenle besleme stoğunun kurutulması gerekmez. Subkritik su ortamının bir başka özelliği de biyokütlenin inorganik kısımlarını yıkama yeteneğidir, bu nedenle torrefe edilmiş biyokütledeki kül miktarı azalır. Literatür taraması sırasında kanatlı çamuru ile ilgili biyokütle dönüşüm çalışmalarına rastlanmıştır. Ancak, mevcut çalışma, 3 farklı bağımsız parametre ile yanıt yüzey metodolojisi (RSM) kullanarak WT'yi DPS'ye uygulayarak literatüre bir yenilik getirmeyi amaçlamaktadır. Çalışmanın temel hedefi, bağımsız proses parametrelerini RSM yardımıyla optimize ederek maksimum katı verimi ile birlikte mümkün olan en yüksek ısıl değeri elde etmektir. Bu şekilde, farklı deneysel koşullar altında WT'nin, DPS'nin yakıt özellikleri üzerindeki etkileri deneysel olarak araştırılmıştır. Bağımsız proses parametrelerinin DPS'nin yakıt özellikleri üzerindeki etkileri, ürün üzerinde yaklaşık, nihai ve ısıl değer analizleri kullanılarak detaylandırılmıştır.

Çalışma, bir kanatlı kesimhanesinden DPS temini ile başlamış, daha sonra nem içeriğini sıfıra indirmek için numuneler konvansiyonel bir fırında kurutulmuştur. Kurutma sürecini, ASTM standartlarına göre yaklaşık, nihai ve ısıl değer analizleri ile ham DPS'nin karakterizasyonu takip etmiştir. Bir sonraki adımda, WT işlemini gerçekleştirmek için deneyler tasarlanmıştır. RSM, deneyi tasarlamak ve yanıtları en üst düzeye çıkarmak için deney koşullarını optimize etmek için kullanılmıştır. Reaksiyon sıcaklığı (°C), reaksiyon süresi (dk) ve besleme konsantrasyonu (wt%), bağımsız proses parametreleri olarak belirlenmiştir. Yanıtlar, ısıl değer ve katı verimi olarak adlandırılmıştır. Deney çalıştırmalarının sayısı ve bağımsız proses parametrelerinin düzeyi Box-Behnken Design tarafından ayarlanmıştır. On beş tasarım deneyi ve bir optimizasyon deneyi dahil olmak üzere 316 L çelikten yapılmış laboratuvar ölçekli bir kesikli reaktörde on altı deney yapılmıştır. Daha sonra, karakterizasyon işlemi için torrefe edilmiş DPS (TDPS) toplanmıştır. WT, DPS'nin reaktöre distile su ile yüklenmesi önceden belirlenmiş bir konsantrasyonda (10:30:50wt%) başlatılmıştır. Karıştırıcı hızı, karıştırma sırasında 100 rpm hızında sabit tutulmuştur. Gerekli inert reaksiyon atmosferi, hava tamamen boşaltılana kadar kapalı reaktöre 1 bar basınçta nitrojen verilerek karşılanmıştır. Basınç, ısı kaynağı tarafından otomatik olarak oluşturulan kritik altı basınç aralığında tutulmuştur. Reaksiyon sıcaklıkları istenen (180:230:260 ℃) seviyelere yaklaştığında, reaktör önceden belirlenmiş (20:40:60 dk) reaksiyon zaman aralıklarında tutulmuştur. Daha sonra reaktör, oda sıcaklığına düşene kadar soğuması için bir buz banyosuna daldırılmıştır. Soğutma işleminden sonra ürünler reaktörden toplanmıştır. TDPS ve sıvı ürünler, 10µm gözenek boyutuna sahip bir filtre kağıdı yardımıyla birbirinden ayrılmıştır. Elde edilen TDPS daha sorna, yaklaşık ve nihai analizlerde hatalı sonuçlara yol açabilecek olası reaksiyon ihtimallerini ortadan kaldırmak için bir kurutma işlemine tabi tutulmuştur. Sonuçlar için yüksek güvenirlik sağlamak ve yanıtları tahmin etmek için varyans analizi (ANOVA) gerçekleştirilmiştir. Son olarak, süreç parametrelerinin bağımsız ve interaktif etkileri araştırılmıştır.

WT proses sonuçları ile ilgili olarak, ısıl değer ve katı verimi üzerinde en belirgin etkiye sahip parametreler, besleme konsantrasyonu ve ardından reaksiyon sıcaklığı olmuştur. Bu nedenle yanıtlar üzerinde en az etkili olan parametre reaksiyon süresi olarak belirlenmiştir. Alkali metaller reaksiyon sırasında katalizör görevi yaptığından, besleme konsantrasyonunun baskın etkisi biyokütledeki alkali metal miktarı ile açıklanabilir. Reaksiyon sıcaklığının yanıtlar üzerindeki etkisinin reaksiyon süresinden daha yüksek olmasının nedeni, bir termal bozunma tepkimesi için birinci dereceden hız yasası ve Arrhenius denklemi yardımıyla açıklanabilir. Proses parametrelerinin yanıtlar üzerindeki etkisi ve birbirleri arasındaki interaktif etkiler, iki ve üç boyutlu kontur grafikleri ile ortaya konmuştur. Her üç parametrenin de yanıtlar üzerindeki etkisini tek bir kontur veya üç boyutlu çizim ile temsil etmek mümkün olmadığından, parametrelerden biri, değişen iki parametre ile optimum seviyede tutulmuştur. Ayrıca, ağırlıkça %83.31 katı verimi ile en yüksek ısıl değer (28867.0 J/g), 280 °C, %50 ve 60 dakika koşullarında elde edilirken, maksimum CV ve SY için optimum koşullar 268°C reaksiyon sıcaklığı, %50 besleme konsantrasyonu ve 47 dakika reaksiyon süresi olarak belirlenmiştir. Varyans analizi sonuçlarına göre, yanıtlar için modelin p değerleri, analizin güven düzeyi olan 0,05'ten küçük bulunmuştur. Bu nedenle, modellerin istatistiksel olarak anlamlı olduğu tespit edilmiştir. Öte yandan, yanıtlar için uyumsuzluk p değerleri 0,05'ten yüksek bulunmuş olup, verilerin modellerle uyumlu olduğu sonucuna varılmıştır. Ayrıca CV ve SY için modellerin korelasyon katsayıları sırasıyla, 95.05%, %97.02 olarak bulunmuştur. Bunun yanında, korelasyon katsayıları modellerde yüksek doğruluk olduğunu ifade edecek kadar yüksektir.

Yaklaşık analiz sonuçları göz önüne alındığında, sabit karbonun ağırlıkça %7.41'den %11.7'ye yükseldiği ve uçucu maddenin ağırlıkça %67.5'ten %66.1'e hafifçe düştüğü bulunmuştur. Ayrıca, TDPS'deki kül miktarı ağırlıkça %25.09'dan %22.18'e düşmüştür. Nihai analizi sonuçlarına göre ise, karboksilasyon reaksiyonlarının bir nedeni olarak O/C'nin atomik oranının 0.158'e gerilediği rapor edilmiştir.

Sonuç olarak, bu çalışmada uygulanan yöntem ile tüm parametrelerin CV'yi arttırdığı, reaksiyon sıcaklığı ve süresinin ise SY'yi azaltma etkisine sahip olduğu rapor edilmiştir. Verilerin analizine göre optimum koşullarda kül, O/C ve toplam katı madde, sırasıyla %11.59, %6.51, ve %14.80 oranında azalmış, ancak CV %7.75 artmıştır. Sonuçlar göz önüne alındığında, TDPS'nin yakıt özelliklerinin yükseldiği ve daha verimli bir katı yakıt haline geldiği ortaya çıkmıştır. Ayrıca karbon oranındaki artış, oksijen içeriğindeki azalma ve kül miktarı, TDPS'yi kömür benzeri bir yapıya dönüştürmüştür. Bu çalışmanın, gelecekteki çalışmalar için WT'nin çeşitli biyokütleler üzerine etkisnin daha ayrıntılı bir şekilde incelenmesine, ve daha geniş uygulama alanına yol açabileceğine inanılmaktadır.

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LIST OF ABBREVIATONS

C	: Carbon
H	: Hydrogen
N	: Nitrogen
S	: Sulphur
O	: Oxygen
WT	: Wet Torrefaction
DT	: Dry Torrefaction
DPS	: Dewatered Poultry Sludge
TDPS	: Torrefied Dewatered Poultry Sludge
TDPS-XX-YY-ZZ	: Torrefied Dewatered Poultry Sludge-Reaction Temperature- Reaction Time- Feed Concentration
CV	: Calorific Value
SY	: Solid Yield
HHV	: Higher Heating Value
FC	: Fixed Carbon
VM	: Volatile Matter
RSM	: Response Surface Methodology
LB	: Lignocellulosic Biomass
NLB	: Non-Lignocellulosic Biomass
SCWG	: Supercritical Water Gasification
SW	: Slaughterhouse Waste
ASTM	: American Society for Testing and Materials
TGA	: Thermogravimetric Analysis
R^2	: Correlation Coefficient
R^2_{Adj}	: Adjusted Correlation Coefficient
p-value	: Probability Value
F-value	: Variance of group means

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1. INTRODUCTION

1.1. Problem Identification

As a consequence of the uncertainty of remaining oil and coal resources and their devastating effects on environmental and human health, renewable energy sources have drawn a lot of attention recently. Biomass is currently the most widely used renewable energy source, and it has a great deal of potential to replace fossil fuels. Biomass can be transformed into chemicals and materials, whereas other renewable energy sources can only provide heat and power. Biomass as an energy source helps to minimize CO_2 emissions, improve energy security, and promote long-term development. However, due to the inherent fuel properties limitations of biomass such as high oxygen and ash content, heterogeneity, and low calorific value, utilizing it as an energy source is not practical. Because of these disadvantages, converting biomass to heat and power is difficult. They also raise the cost of processing, transporting, and storing fuel. Besides, mentioned drawbacks lower the efficiency of the biomass conversion methods such as gasification and pyrolysis.

Barriers to using biomass as an energy source can be overcome with a thermochemical treatment of torrefaction. Employing torrefaction to biomass eliminate or reduce the aforementioned disadvantages of using biomass as fuel or raw material for conversion methods. Torrefaction can be done in two ways: dry or wet. Thermochemical treatment of biomass in an inert environment at atmospheric pressure and temperatures of 200–300 °C is known as dry torrefaction (DT). Treatment of biomass in a hydrothermal medium, or hot compressed water, at temperatures of 180–260 °C is known as wet torrefaction (WT). When compared to original biomass, both torrefaction methods generate hydrophobic solid fuels with significantly improved heating value with reduced ash and oxygen content.

DT for energy applications has been the subject of intense research and development over the last decades. Similar studies for WT, on the other hand, are still few since it is a novel technique compared to DT. As a result, knowledge of the WT process such as operating parameters effects of temperature, holding time, feed concentration. Besides, the fuel characteristics of WT products are limited. However, literature studies have shown that wet torrefaction is more effective than dry torrefaction on fuel properties. Therefore, WT has recently attracted the attention of scientists and the number of studies on it has increased.

1.2. Study Objectives

The main aim of the current study is to improve the fuel properties of biomass, which is an organic renewable energy source that will reduce fossil fuel dependence. To achieve our ultimate goal wet torrefaction is implemented to dewatered poultry sludge (DPS). The influence of the operating parameters on solid yield and calorific value was investigated and optimized.

More specifically, project objectives can be as follow:

- Determining the operating (Input) parameters that are most influential on calorific value and solid yield of biomass.
- Determination of the influence of operating parameters. Using the Pareto charts the individual effect of reaction temperature, time, and feed concentration on solid yield and calorific value.
- Determination of the interactive influence of operating parameters. 3-D surface plots and contour plots were utilized to investigate the interactive effects of reaction temperature, time, and feed concentration on solid yield and calorific value.

- Considering the solid yields and calorific values of wet torrefied DPS. The optimum condition was determined through Response Surface Methodology (RSM).
- Determining ash, fixed carbon, and volatile matter content and making a comparison between raw and wet torrefied DPS through proximate analysis.
- Determining Carbon (C), Hydrogen (H), Nitrogen (N), Sulfur (S), and Oxygen (O) content and making a comparison between raw and wet torrefied DPS through CHNS analyzer.

It is aimed to fill the gap in the literature by reaching the research goals. The fact that the selected biomass has not been subjected to wet torrefaction in any study before will provide important information to the literature.

1.3. Biomass as Energy Source

One of the most difficult technical problems in engineering is meeting the need for efficient and clean energy sources. Fossil fuels meet the majority of present energy demand; however, they are extremely dangerous to the environment, contributing to global warming through greenhouse gas emissions. Furthermore, fossil fuels are non-renewable, therefore reserves will eventually deplete. Any reduction in emissions improves energy security and reduces reliance on finite fossil fuel supplies. As a result, renewable energy sources have received a lot of attention. Biomass, solar, geothermal, wind, and hydropower are the most important and studied renewable energy sources. Biomass is any organic material originating from plants or animals that are alive or has been dead for a brief length of time (Mamvura & Danha, 2020). Biomass is the only renewable organic resource that can be found in abundance among them. In addition to having a large feedstock, biomass combustion is carbon neutral, in comparison to fossil fuels.

Since it has a short carbon cycle, biomass is not directly contributing to the total CO2 emission into the atmosphere (Bilgen et al., 2015).

Biomass is a carbon-rich, renewable resource that can be used to generate heat, power, fuels, chemicals, and other bio-products (Ong et al., 2021). According to International Energy Agency (IEA), renewable energy sources contributed to the total world primary energy supply by 14.1% in 2018. The portion of biomass within the total renewable sources is 9.5%, making it the fourth-greatest contributor to the world energy supply. Furthermore, the IEA 2019 report predicted that thanks to sustainable developments, renewable energy sources will contribute 20.19 percent of the world's primary energy demand by 2030 (IEA, 2019).

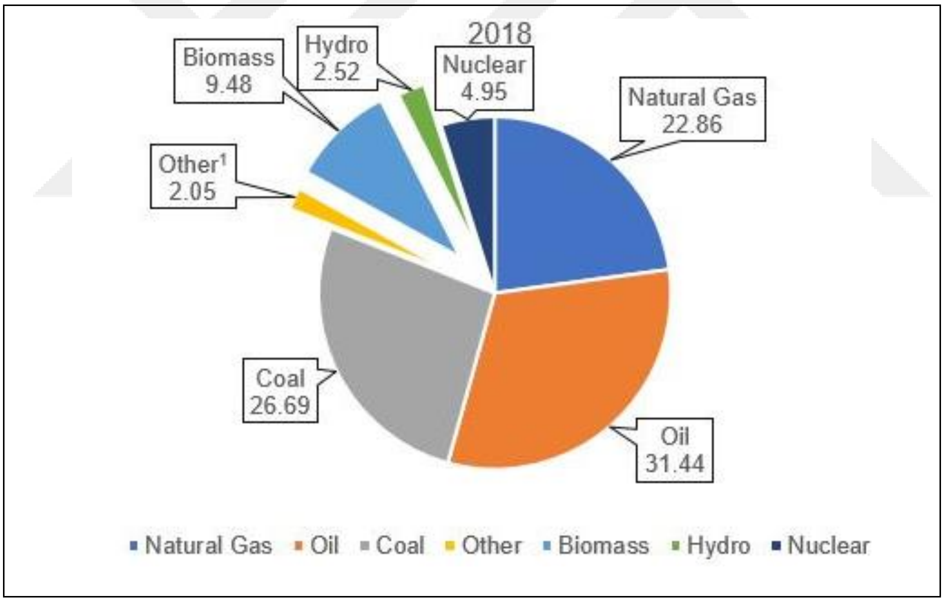

Figure 1. 1. Global biomass energy contribution compared with other energy sources in 2018 (IEA, 2019). [1] Includes geothermal, solar, wind, tide/wave/ocean, heat, and other sources

1.4. Classification of Biomass

As mentioned earlier, biomass is a scientific term for any organic matter that is alive or has just died. As a result, biomass can be used to describe a wide variety of products obtained from living organisms. A simple method, according to ISO 17225-1:2021, can be used as a classification. Biomass for bioenergy can be divided into groups by where it originates from or what industry it produces from (see in Figure 2) (ISO, 2021; Islas et al., 2019):

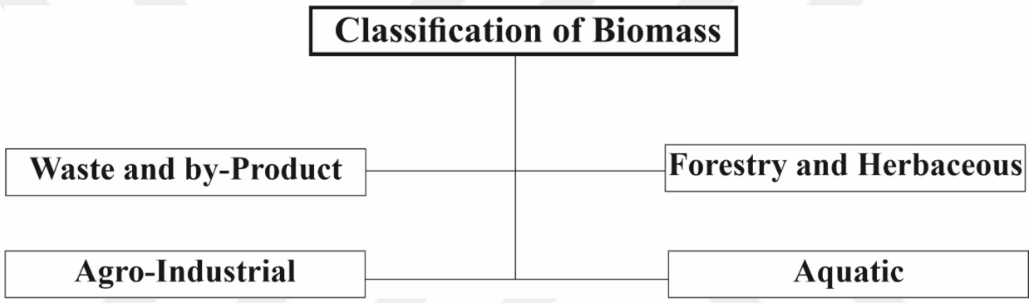

Figure 1. 2. Classification of Biomass

1.4.1. Forestry and Herbaceous Biomass

Wood from forests and other wooded land are examples of forestry biomass. Woody biomass can be obtained through logging, pruning, and brush cleaning, etc (Ciria & Barro, 2016). Plants with stems and leaves that die at the end of the growing season are known as herbaceous biomasses (Rosendahl, 2010). Woody and herbaceous biomasses are considered lignocellulosic biomass since the chemical composition consists of plant fibers. Lignocellulosic biomass (LB) is a plant-based renewable energy resource. Mainly, LB consists of cellulose (30-50 wt%), hemicellulose (20-40 wt%), and lignin (15-25%) (Liang et al., 2021). Wood-based fuel accounts for the largest bioenergy portion of the world.

1.4.2. Agro-Industrial Biomass

Since agro-industrial biomass has a similar chemical composition to forestry biomass, they are also considered lignocellulosic biomass. Agro-Industrial biomasses are obtained during the production of food, for example, bagasse, husk, oil, and cereal crops (Islas et al., 2019). Agro-Industrial biomass accounts for the second-largest biomass feedstock after the wood-based biomasses (Sánchez et al., 2019).

1.4.3. Waste and by-Products

Waste and by-products originated from agricultural, forestry, and industrial human activities. Wastes are often difficult to dispose of as they are pathogenic. Therefore, it is more efficient to use them as an energy source (Kamizela et al 2021). Industrial and agricultural wastes and by-products involve municipal solid waste, sewage sludge, slaughterhouse sludge, etc. Furthermore, wastes include animal and human wastes such as bones, blood, skin, manure, etc (Zhai et al 2021).

The need to modify existing technologies for treating waste biomass that is viable in both developed and developing countries is driven by the growing global population. Especially in developing countries, and the requirement for improved sanitation to prevent the infection by microbial diseases. Furthermore, the global concern about climate change emphasizes the importance of keeping a low carbon footprint (Xiao et al., 2022). One of the most abundant waste biomass is slaughterhouse waste (SW). SW constitutes the inedible parts of animals derived from the production of meat, as well as blood and other animal by-products. SW is not only polluting the environment but also poses a danger of the transition of disease from animals to humans when it is used as fertilizer. SW pose danger to animal and human health since these wastes contain parasitic, bacterial, and viral pathogens. There are several available biological and thermochemical methods to disposal or convert into efficient fuel (I.H. Franke-Whittle and H. Insam, 2013; A. Ferreira et al., 2017).

1.4.4. Aquatic Biomass

Algaes and aquatic plants are a member of aquatic biomass. Algaes are divided into macro and microalgae (Tamayo Tenorio et al., 2018). In general, their moisture content is higher compared to other types of biomass, thus they have lower calorific value and energy density (Poomsawat & Poomsawat, 2021). Nevertheless, they do not occupy farmland compared to woody and herbaceous biomasses, besides their growth rate is higher than theirs (Mu et al., 2021).

1.5. Biomass Conversion Methods

In this section, main biomass conversion pathways are described, and their products are explained. Bioenergy is defined as the energy potential of biomass. It can be converted into liquid, solid and gaseous biofuels for bioenergy production through thermochemical, biochemical, physical methods (Naik et al., 2009). Thermochemical conversion methods include combustion, gasification, pyrolysis, and torrefaction. Fermentation and anaerobic digestion are biochemical conversion methods, whereas briquetting and distillation are conducted through physical methods (Demirbas, 2009; Ibrahim and Akilli, 2019).

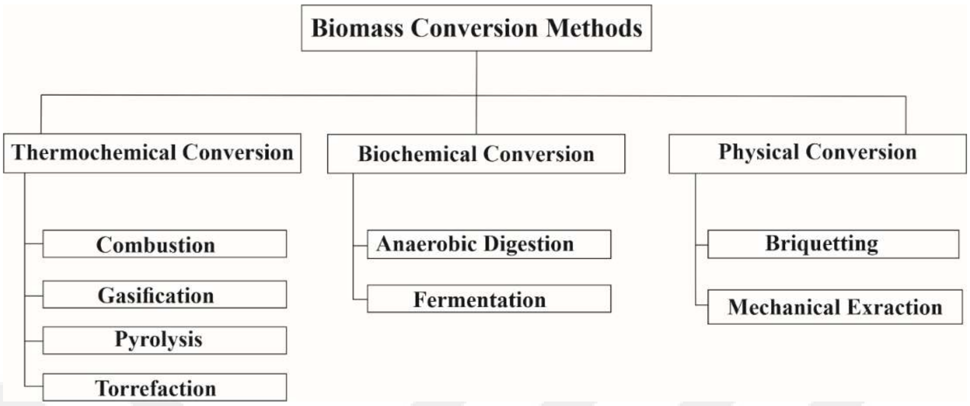

Figure 1. 3.Biomass Conversion Methods

1.5.1. Thermochemical Conversion

Heat and pressure are used with or without a catalyst to transform the biomass into a valuable energy source in thermochemical conversions. Any sort of biomass can be utilized as a thermochemical conversion raw material. Forest and agro-industrial residues, nonfermentable biorefinery byproducts, and some forms of organic municipal wastes are all examples. The products of thermochemical conversion can be utilized to make a variety of fuels and chemicals that can be used to replace petroleum and coal-based substances (Bajpai, 2020). Thermochemical conversion methods are conducted in minutes or seconds, thus they are very rapid processes compared to biochemical ones. Moreover, reactor volumes are lower compared to reactors used in biochemical processes. However, energy input in thermochemical methods is much more in thermochemical processes. (Seo et al., 2022).

1.5.1.1. Combustion

Combustion, often known as burning, is a chemical process that occurs when a fuel reacts with oxygen in the presence of air with the emission of heat, the products are carbon dioxide and water. The combustion process is characterized by a series of exothermic processes. The energy contained in a fuel's chemical bonds is transformed into thermal energy, which can be used in our homes to produce heat or in a power plant to generate the necessary steam for turbines to produce electricity and heat (Abuelnuor et al., 2014). Drying, devolatilization, gasification, char combustion, and gas-phase oxidation are the key process stages. The combustion of biomass or biogenic residues is established on an industrial scale and is applied worldwide as the most common energetic utilization pathway for biomass (Nussbaumer, 2003).

1.5.1.2. Gasification

Gasification is a multi-stage process such as moisture removal, devolatilization, partial oxidation, followed by gasification, and by-products. Gasification can be studied based on the gasifier type, operating pressure, temperature, catalyst presence, and gasifying agent utilized (Liu et al., 2022). CO, CO2, H2O, H2, CH4, and other gaseous hydrocarbons made up the production of gas. The by-products are tars, char, inorganic components, and ash (Zabaniotou et al., 2014). There are two different types of gasification, one of them is conventional gasification and the other one is supercritical water gasification (SCWG). Due to the unique properties of supercritical water SCWG attracted attention. Supercritical water has a lower dielectric constant, therefore its polarity is decreased and acts as an organic solvent (Yan et al., 2020).

1.5.1.3. Pyrolysis

Pyrolysis is a potential process for disposing of sewage sludge and biomass wastes. Pyrolysis is the degradation of solid biomass or fuel by heat energy. Degradation processes occur in an inert atmosphere, oxygen-free, to produce condensable vapors, permanent gases, and solid residues known as bio-char that contain ash and fixed carbon (Soria-Verdugo, 2020). This bio-oil can be utilized as a fuel in energy-generating combustion engines and turbines. The solid residue has been intensively explored for usage as a home fuel as well as in industrial applications as a reducing agent in metallurgy or as a raw material for products like fertilizers (Marulanda et al., 2019). At room temperature, condensable vapors can be easily transformed into liquid form or bio-oil. Permanent gases consist of CO, CO_2, and CH_4 which can be used in renewable energy applications. Depending on the severity of the pyrolysis process, biochar contains different fractions of unconverted solids, inorganic elements called ashes, and carbonaceous residues (Dhyani & Bhaskar, 2019).

1.5.1.4. Torrefaction

Torrefaction is a thermochemical conversion technique for converting biomass into biochar or hydrochar depending on the technique of torrefaction whether it is wet or dry. Torrefaction produces solid biofuel as the main products, with liquids and gases as by-products. Biochar or hydrochar is a carbon-rich solid fuel produced from the thermal composition of organic feedstock in an inert atmosphere and temperature range within 200-300 °C (Ong et al., 2019). These solid fuels can be also produced through slow pyrolysis. However, biochar produced with pyrolysis has a lower calorific value compared to torrefied ones. Therefore, utilizing the solid products of pyrolysis as fertilizer rather than an energy source is more suitable (Choo et al., 2020).

1.5.2. Biochemical Conversion

The enzymes of bacteria and other microorganisms are used in biochemical conversion processes to degrade biomass. Microorganisms are used to perform the conversion process in the majority of cases: anaerobic digestion and fermentation. The goal of pretreatments in biomass biochemical conversion technologies is to aid in achieving optimal conversion effects, not to produce final products, which is the significant difference between the aforementioned biomass conversions. Considering the large scale, biochemical conversion processes are efficient, clean, and pure compared to the thermochemical conversion process. However, the required time for chemical and biological reactions in biochemical conversion processes is much higher than in thermochemical conversion processes (Chen & Wang, 2017; Sam & Barik, 2019).

1.5.2.1. Anaerobic Digestion

Organic matter is degraded with the help of a collection of specialized microorganisms in the anaerobic digestion process. The anaerobic digestion process is classified into two categories based on the dry matter content of the feedstock: wet state and solid-state, with four steps in between hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Tayibi et al., 2021). During the digestion processes, the organic materials are converted into fermentable sugars by the hydrolysis process. Through the microorganisms, these sugars are converted into H_2, CH_4, CO_2, and other by-products (Marulanda et al., 2019).

1.5.2.2. Fermentation

Similar to Digestion, microorganisms are the key materials that provide a path to obtain value-added biofuel. Microorganisms are utilized in biomass fermentation to transform feedstock into biofuels like bioethanol. Biomasses are commonly utilized as feedstocks in the fermentation of simple sugars into bioethanol or biobutanol to make ethanol. The presence and removal of various by-products of hydrolysis processes and yeast metabolism, such as hydroxymethylfurfural, are the key operational parameters effective on ethanol yield and fermentation efficiency. As a result, choosing the right fermentation medium and yeast, and eliminating the fermentation by-products are all effective ways to raise fermentation yield (Wei et al., 2020).

1.5.3. Physical Methods

Through the physical conversion of biomass, higher energy is obtained in a lower volume, called densification. The requirement of input energy is relatively lower compared to other conversion methods, since there is no change in the chemical structure of biomass particles. By using mechanical power and heat energy, the energy per unit volume of biomass is increased, so that storage and transportation of biomass processes become more efficient (Kpalo et al., 2020).

1.5.3.1. Briquetting

Briquetting is the process that transforms waste biomass from agriculture, forestry, and other industries that generate waste into a completed product, such as briquettes. When compared to raw biomass, briquettes offer significant energy savings. Briquetted biomass has lower sulfur and ash content than raw biomass, and moreover, the moisture content is less. Solid bio-fuels with increased energy density and improved fuel properties are obtained as a product of the briquetting technique (Ibitoye et al., 2021). One of the important factors in most briquetting applications is the presence of a binder. The moisture content of the biomass, its chemical structure, and operational parameters during application affect the amount of binder (Fehse et al., 2021).

1.5.3.2. Mechanical Extraction

Since bio-oils have an important place in the search for a sustainable energy source, the essential oils contained in biomass have attracted attention as a renewable energy source. Mechanical extraction is conducted using cylinder-hole or strainer-type screw presses crushed or sieved biomass that thermally pretreated. Because of the increased contact area, pore opening, cell wall cracking, and reduction of oil viscosity and moisture, size reduction and thermal pretreatment improve oil extraction (Yate et al., 2020).

1.6. Biomass Torrefaction Technology

Biofuels obtained with one of the conversion methods supply a significant amount of bioenergy. However, biomass as a fuel, with the help of conversion processes, is not straightforward. As a solid fuel, biomass presents similar characteristics to that of coal. Although there are similarities, biomass has inferior fuel properties to coal. Resulting from the inherent properties of biomass, it has low bulk and energy density, high moisture and oxygen content, low calorific value, heterogeneity, and poor grindability compared to coal (Bach and Skreiberg, 2015). High moisture and oxygen content reduces the calorific value and efficiency of the conversion processes while requiring a drying process which increases the cost. On the other side, high moisture content causes handling, transportation, and storage challenges due to the degradation of organic compounds. Moreover, while low bulk and energy density require high feeding capacity, heterogeneity brings about a wide variation in the fuel properties. Therefore, the biomass resources are distributed more evenly but less concentrated compared to coal (Vassilev et al., 2015; Acharya et al., 2015). To overcome the mentioned drawbacks and improve the efficiency of the applied method, biomass can be pretreated and upgraded with the torrefaction process. Wet and dry torrefaction processes are available to improve the physical and chemical properties of the raw biomass (Zheng et al., 2015).

1.6.1. Dry Torrefaction

Dry torrefaction is a suitable process to improve the fuel properties of biomass and is also called mild pyrolysis. In general, DT is conducted at a temperature range of 200°C to 300°C with a slow heating rate (<50°C/min) in an inert atmosphere, the residence time of DT varies from study to study but generally 15 to 60 min (M.N. Cahyanti et al., 2020). The main product of DT is carbon-rich biochar, byproducts are condensable vapors and permanent gases such as CO,

CO_2, and CH_4. The solid product obtained after the torrefaction process has a high energy density and low moisture content when compared to the raw biomass (Jaideep et al., 2021). However, the ash content of dry torrefied biomass is higher than raw and wet torrefied ones (Zhang et al., 2019). The disadvantages and limitations of DT are discussed in the Previous Studies section.

1.6.2. Wet Torrefaction

WT is performed in a hydrothermal media which is obtained by mixing distilled water and biomass in an appropriate ratio, at a temperature range between 180-260°C. Similar to the DT, the heating rate of WT is slow, and the reaction atmosphere is inert. Inert reaction atmosphere takes place through initial pressuring with N_2. WT pre-treatment is usually completed in between 5 to 240min (Q.-V. Bach et al., 2013). The reaction pressure of WT is autogenerated, which means that pressure depends on reaction temperature (X. Lu et al., 2012).

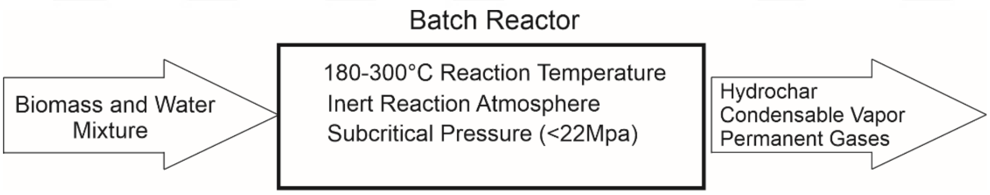

Figure 1. 4. Layout of Wet Torrefaction Process

The state of water between 100°C (boiling point) and 374°C (critical point) under a sufficient pressurized condition to maintain the liquid state of water is known as subcritical water (Sarker et al., 2021). Subcritical water is considered one of the environmentally friendly solvent for organic compounds in a variety of industrial and commercial applications. Water qualities such as viscosity, diffusivity, polarity, dielectric constant, and density change as temperature rises (see in Figure 1.5.) (Zhang et al., 2020). Subcritical water brings about a variety of chemical transformations, including efficient mass transfer and hydrolytic processes, because of these changes in thermo-physical characteristics.

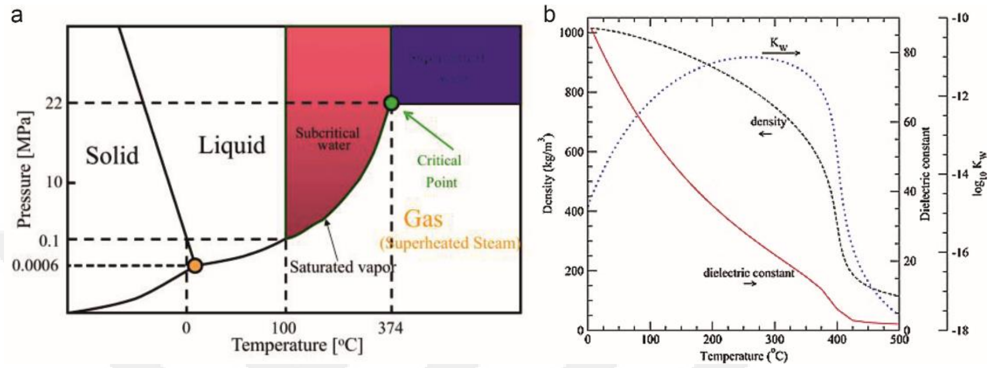

Figure 1.5. (a) Phase Diagram of Water (b) Effect of temperature on subcritical water (Zhang et al., 2020)

The terminologies of WT and hydrothermal carbonization (HTC), which is a similar treatment to WT, can be found in literature as substituted with each other (B. Acharya et al., 2015). However, the aims of these pre-treatments differ from each other. WT aims to enhance the efficiency of subsequent treatment or upgrading fuel properties of raw biomass, whereas HTC aims to transform biomass to charcoal which can be used as both fuel and fertilizer.

2. PREVIOUS STUDIES

2.1. Wet Torrefaction Studies

The wet torrefaction (WT) or hydrothermal carbonization (HTC) process has been implemented to different types of biomass, e.g. lignocellulosic and non-lignocellulosic. The majority of the WT process is based on lignocellulosic biomass, and studies on the WT application to non-lignocellulosic biomass are limited. The WT process also differs depending on the method and technology used. Conventional or Directly, Catalytic, and Microvawe Assisted WT are examples of the type of WT processes. Catalyst and microwave heating methods have been used in many studies to improve the physical and chemical properties of the product of WT or HTC and to increase the efficiency of the process. Regardless of the method used and the type of biomass, there are also some differences according to the purpose of performing the WT treatment. Studies in the literature have shown that the pyrolysis and gasification processes of torrefied biomass are more efficient than raw biomass.

2.1.1. Wet Torrefaction of Lignocellulosic Biomass

Cellulose and hemicellulose (carbohydrate polymers), lignin, and a minor proportion of extractive acid, salts, and minerals constitute lignocellulosic biomass (see in Figure 6) (Muktham et al., 2016). The content of these elements varies depending on the plant type. Hardwood, for example, contains more cellulose, but wheat straw and leaves have more hemicellulose (Kumar et al., 2009).

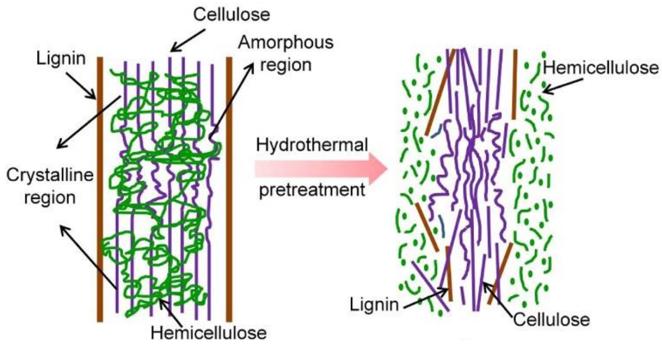

Figure 2.1.Structure of Lignocellulosic Biomass (Muktham et al., 2016)

In order to improve the fuel properties of almond-tree prunings (ATP), lignocellulosic biomass, Aguado et al. (2020) conducted wet torrefaction experiments. They investigated the effect of reaction temperature and time on wet torrefaction of ATP. Temperature and time are varying between 175-300 °C and 10-60 min, respectively, in a high-pressure batch reactor. To represent and easily understand the level of input parameters they evaluated the severity factor according to reaction temperature and time. The calorific value of the ATP was increased to nearly 30 MJ/kg at the highest severity factor. On the other hand, the calorific value of 24 MJ/kg was achieved at the optimum severity factor of 5.78. Furthermore, they reported that the elemental composition and other fuel properties such as ash and fixed carbon content were examined. They concluded that higher temperature and time were upgraded the fuel properties of ATP.

Soh et al. (2021) investigated the effect of wet torrefaction on physical, chemical and fuel properties of two different biomass; empty fruit bunches (EFB), and oil palm trunks (OPT). Input parameters were selected as temperature (180, 210, and 240 °C) and time (2, 2.5, and 3 hours). They reported that temperature is more effective on wet torrefaction of EFB and OPT compared to time. Besides, results of Fourier Transform Infrared (FTIR) spectra of raw and wet torrefied EFB and OPT showed that hydroxyl and carboxyl groups significantly reduced with wet torrefaction. They also reported that the results of the scanning electron microscope

(SEM) indicate wet torrefaction caused spiky globules on the surface of EFB and OPT. Therefore, the surface area and porosity were increased.

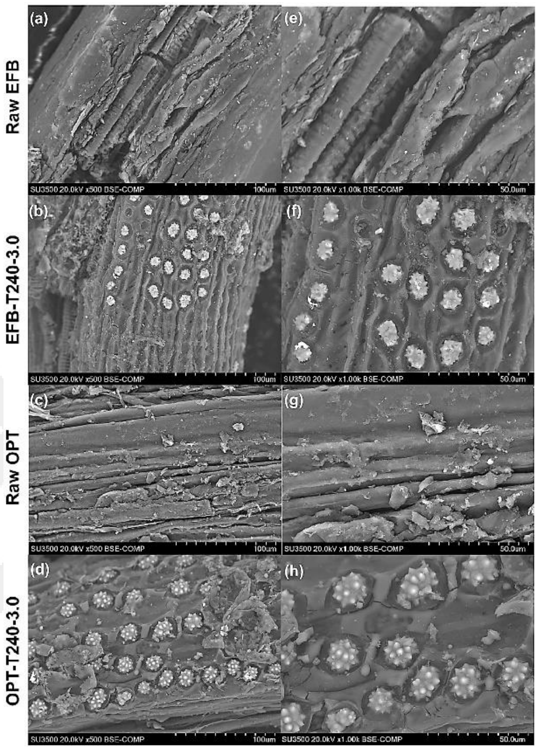

Figure 2.2. Scanning electron microscopy (SEM) images of raw and wet torrefied EFB and OPT (Soh et al. 2021)

Another study was conducted by Yang et al. (2015), who employed the wet torrefaction on different biomasses *Humulus lupulus* (HL), *Plumeria alba* (PA), and *Calophyllum inophyllum* (CIL) with different weight ratios. They reported that the reactivity of cellulose and hemicellulose depends on biomass species and the weight ratio of biomass. Considering their results, lignin is the main component that affects solid yield. According to elemental analysis results, wet torrefaction increased the carbon content of biomasses as temperature increased, so the H/C and O/C atomic ratios decreased. They concluded that the calorific value of biomasses elevated and can be comparable with commercial coals.

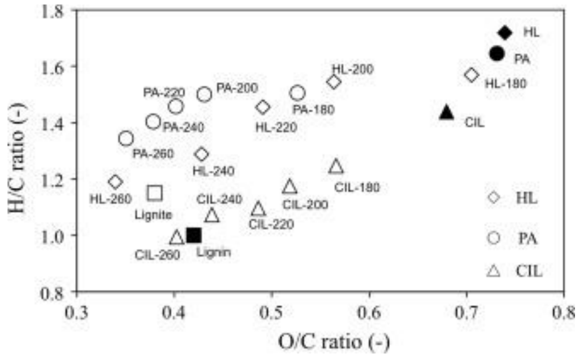

Figure 2.3. Van Krevelen diagram of biomasses, solid fuels, lignite as well as lignin (Yang et al. 2015)

2.1.2. Wet Torrefaction of Non-Lignocellulosic Biomass

Biomass includes animals, microorganisms, a portion of plants, and materials derived from them, in addition to plants and their derivatives. Non-lignocellulosic biomass is described as biomass that contains proteins, lipids, saccharides, inorganics, and a portion of lignin and cellulose. However, due to their complex and varied components, non-lignocellulosic biomasses such as sewage sludge, manure, industrial sludges, municipal waste, and others still face significant problems in terms of value-added disposal and utilization. Because of its higher amount of heavy metals and heteroatoms, the non-lignocellulosic biomasses pose a bigger threat to the environment than lignocellulosic biomass (Tian et al., 2014; Li et al., 2017).

Kim et al. (2014) experimentally investigated the hydrothermal carbonization (wet torrefaction) of the anaerobically digested sewage sludge. They reported that the highest higher heating value of 22.4MJ/kg was obtained at 280 °C, however the optimum temperature is stated as 220 °C in terms of higher heating value and product yield. Furthermore, carbon and fixed carbon content of wet torrefied were increased due to dehydration and decarboxylation reactions.

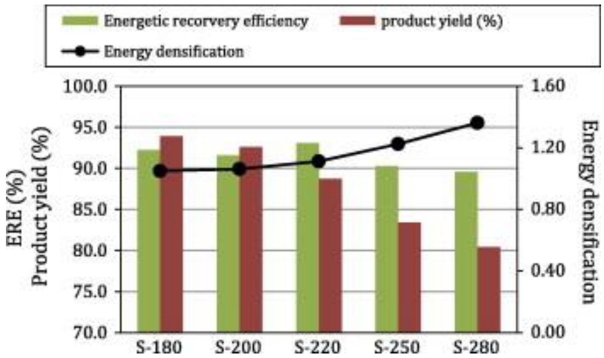

Figure 2.4. Wet torrefaction effect on energetic recovery efficiency (ERE) and product yield (Kim et al., 2014)

Animal manure has been studied extensively and has been used as an energy source for a long time due to its high solid fuel properties. Li et al. (2021) conducted a study on the effects of co-hydrothermal carbonization (co-wet torrefaction) on a mixture of the swim (SM) and chicken manures (CM) with high solid fuel potential. Their findings showed that the mutual interaction of reaction intermediates from various types of animal manure increased hydrochar formation. Furthermore, because of the improved re-polymerization and carbonization, the synergistic effects during the co-HTC were advantageous to N and C enrichment in the hydrochar. They concluded that the co-hydrothermal carbonized hydrochar's combustibility was improved in terms of ignition temperature and entire combustion index. Furthermore, according to their Fourier-transform infrared spectroscopy (FTIR) results, the hydroxyl group of hydrochars decreased and hydrocarbon content increased (see in Figure 2.5).

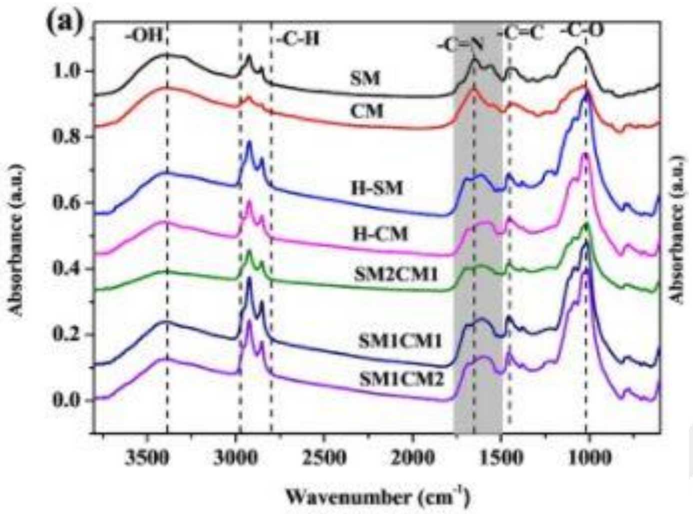

Figure 2.5. FTIR results of the raw and wet torrefied manures (Li et al., 2021)

2.1.3. Microwave-Assisted Wet Torrefaction

When it comes to dielectric materials, microwave irradiation appears to be a viable option for heating. Contrary to conventional conduction and convection, which supply heat by superficial heat transfer, microwave irradiation creates heat inside the material by causing an interaction between the heated object and the applied electromagnetic field (Chen et al., 2012). However, if the material to be heated by the microwave irradiation is heterogeneous, it will cause hot spot formation and intergranular explosion, resulting in a change in material structure (Hu et al., 2008). Overall, the benefits of microwave irradiation for material heating include: lowering heating or pretreating time; offering quick and volumetric heating; immediate start-up and stop of heating; and minimizing reactor size (Gabriel et al., 1998; Jones et al., 2002).

In order to produce biochar, and sugar for bioethanol, two different microalgae species (ESP-31 and FSP-E) were subjected to a microwave-assisted wet torrefaction process in an acid solution by Gan et al (2020). Temperature and time were fixed at 180 °C and 10 min respectively, while the acid solution was varying. According to their result, wet torrefied microalgae in sulfuric and succinic acid solution showed lower ash content compared to wet torrefied ones in phosphorus acid solution. Moreover, they stated that succinic, and phosphorus acid were suitable for biochar production since these acids are organic.

Another study performed by Zhang et al. (2021), in their study corn residues were subjected to a series of microwave-assisted wet torrefaction processes. According to their results, selective heating of microwave radiation significantly increased the calorific value of corn residues. They stated that the Deoxygenation, dehydration, and decarboxylation processes resulted in the increase in carbon content in hydrochar samples, which enhance calorific value. Furthermore, their results indicate that water in the biomass not only absorbed microwave radiation to speed up the heating process, but also washed out ash.

2.1.4. Wet Torrefaction as a pretreatment of Pyrolysis and Gasification

The inherent disadvantages of using biomass as solid fuels are also barriers to other biomass conversion processes such as steam gasification and pyrolysis (Lin et al., 2020; Bahcivanji et al., 2020). It has the potential to provide high conversion efficiency, increased outputs, and the capacity to employ a variety of feedstock without the need for a drying process (Ma et al., 2019).

Gai et al. (2016) conducted a study to investigate the effects of hydrothermal carbonization on the gasification process. Two different samples were utilized for the gasification process in their study one of the sample was obtained from hydrothermal carbonization (hydrochar) and the other one is obtained from the pyrolysis process (pyrochar). According to their approximate analysis results, the fixed carbon ratio increased and the elemental analysis indicated that the carbon, nitrogen, and sulfur ratios increased. Moreover, according to the results of their FTIR analysis, decreasing hydroxyl and carboxyl groups were observed. They concluded that hydrochar steam gasification resulted in greater hydrogen concentrations, yields, and gasification efficiency. Compared to pyrochar, hydrochar gasification produced a higher H2 yield (see in Figure 2.6).

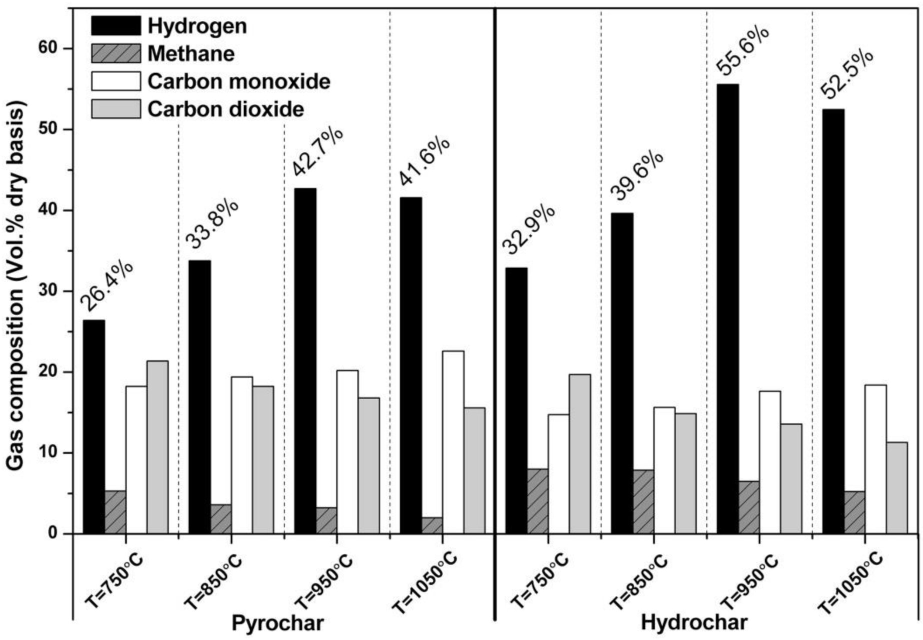

Figure 2.6. Comparison of syngas resulting from gasification of Pyrochar and Hydrochar (Gai et al., 2016)

A different study in which wet and dry torrefaction was applied as a pretreatment before pyrolysis was carried out by Sun et al. (2019). Tobacco stalk (TS) was used as biomass in this study and by employing the wet and dry torrefaction it was aimed that increase pyrolysis yield and efficiency. According to their result activation energy of wet torrefied TS was found to be 49.53 KJ/mol whereas activation energy of dry torrefied TS was found to be 351.43 KJ/mol. They stated that the differences between activation energy of torrefied samples originating from high devolatilization in dry torrefaction. Furthermore, they claimed that adding a catalyst to wet/dry torrefied biochar considerably reduced the pyrolysis activation energy while improving the content of phenol and ketone (see in Figure 2.7).

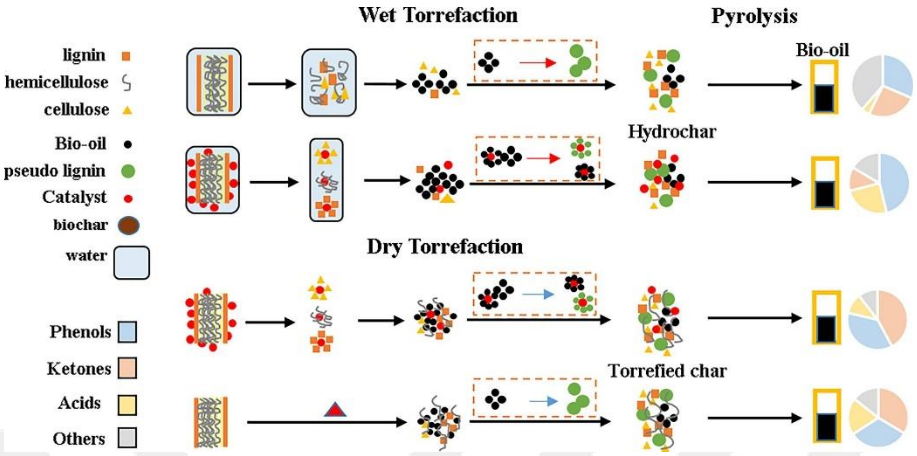

Figure 2.7. Effect of catalyst on wet/dry torrefaction product (Sun et al., 2019)

2.2. Comparison of Wet and Dry Torrefaction

The most fundamental and important difference between wet and dry torrefaction is the moisture content of the feedstock. Dry torrefaction (DT) requires dried feedstock to enhance its fuel properties (Tumuluru et al., 2011). The drying of feedstock is an energy-intensive and high-cost process. The moisture content of the input feedstock must be less than 5–10 wt% for DT to work (Mišljenović et al., 2014). Wet torrefaction (WT), however, is suitable for moist feedstock even the hydrothermal media brings a lot of advantages to WT. Thanks to unique subcritical water properties, the temperature can be used to change the dielectric constant of water, and hence polarity and density to allow for fast extraction of soluble substances (Paini et al., 2021). Furthermore, WT is capable of removing ash from biomass through its hydrothermal media. DT highly devolatilizes the biomass, resulting in high ash content (Ho et al., 2020).

A study, conducted by Wang et al. (2018), has shown that ash removing rate of WT is higher than the DT. They employed the WT and DT on corn stalk in order to compare ash removing performance of them. According to their result, compared with DT, WT removed 98% of the ash with higher oxygen removing efficiency (see in Figure 2.8).

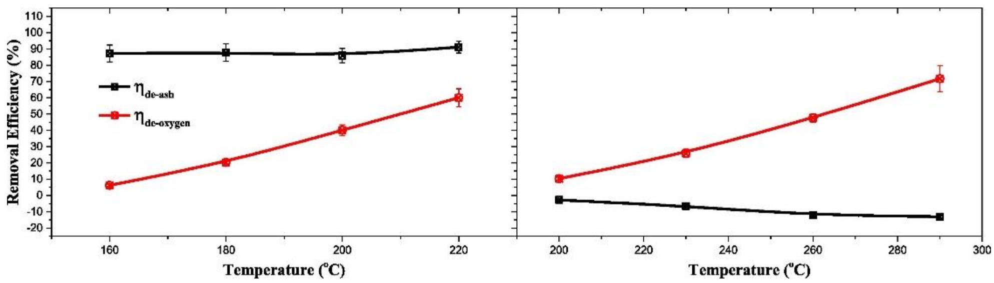

Figure 2.8. Ash and Oxygen removing performance of WT (Left column) and DT (Right column) (Wang et al., 2018)

Another difference between WT and DT is the pelletability of biochar and hydrochar. Bach and Skreiberg (2016) reviewed a study related with comparison of WT and DT. They stated that considering the lignocellulosic biomass (see Figure 2.9), lignin undergoes a modification and result in a more brittle and friable structure in biochar. However, WT does not affect the lignin's nature. Therefore, fibrous hydrochar pellets have more strength compared with biochar. The fact that the structure of biochar is friable and has less fiber causes the need for an external binder during the pelleting process.

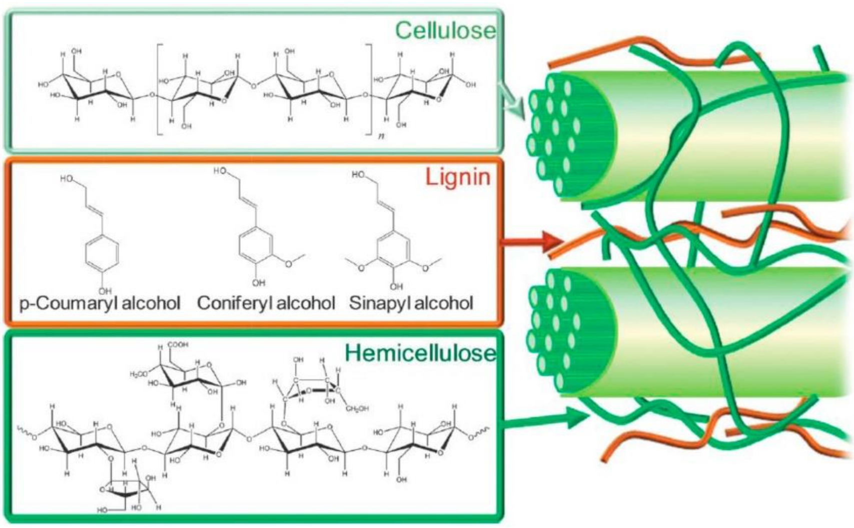

Figure 2.9. Lignocellulosic biomass structure representation (Bach and Skreiberg, 2016)

2.3. Dewatered Poultry Sludge as Bioenergy Source

Through the biomass feedstocks used in the literature, slaughterhouse wastes constitute the inedible parts of animals derived from meat, blood, and other animal byproducts. One of the most abundant slaughterhouse wastes is Dewatered Poultry Sludge (DPS), which consists of offal, bone, blood, and feather. So, DPS pollutes the environment and threatens the transition of disease from animals to humans when used as fertilizer because its wastes contain parasitic, bacterial, and viral pathogens (Eryuruk et al., 2018; Ferreira et al., 2017). To the best of the author's knowledge, only the biochemical methods have been applied to obtain bioenergy from DPS within the available literature (Barca et al., 2015).

During the slaughtering process, about 20% of a poultry bird's total weight is considered as waste. The waste components created by a single bird are seen in Figure 2.11 (Arshad et al., 2018). Organic matter constitutes the slaughtering waste, making it a valuable feedstock for bioenergy production. Crude proteins and lipids are also present in a small amount of slaughtering waste. The feathers are consisted primarily of keratin, which comprises proteins, lipids, and minerals, whereas the heads, legs, and bones contain protein and lipids. Blood, which contains protein and lipids as well as other minor components, is another component of slaughtering waste (Salminen et al., 2002).

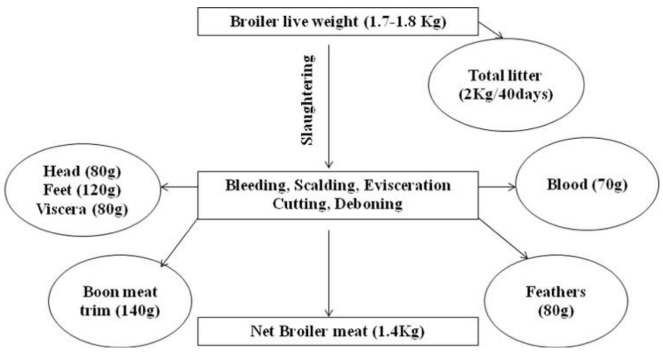

Figure 2.10. Poultry slaughtering wastes and products (Arshad et al., 2018)

There are limited studies that are utilized poultry sludge as raw material in the available literature. The conversion methods employed to poultry sludge are biological, chemical as well as biochemical methods. Yoon et al. (2014) conducted a study on energy recovery from poultry slaughterhouse waste. They reported that methane production per 1000 poultry, through anaerobic digestion, is 35 N m3. Moreover, they classified the slaughterhouse waste and reported their amount on a daily basis. According to their results produced sludge from waste is 2.2 Mg day^{-1} and the total amount of wastewater is 1050 m^3 day^{-1} at a capacity of 100000 heads day^{-1} (see Figure 2.10).

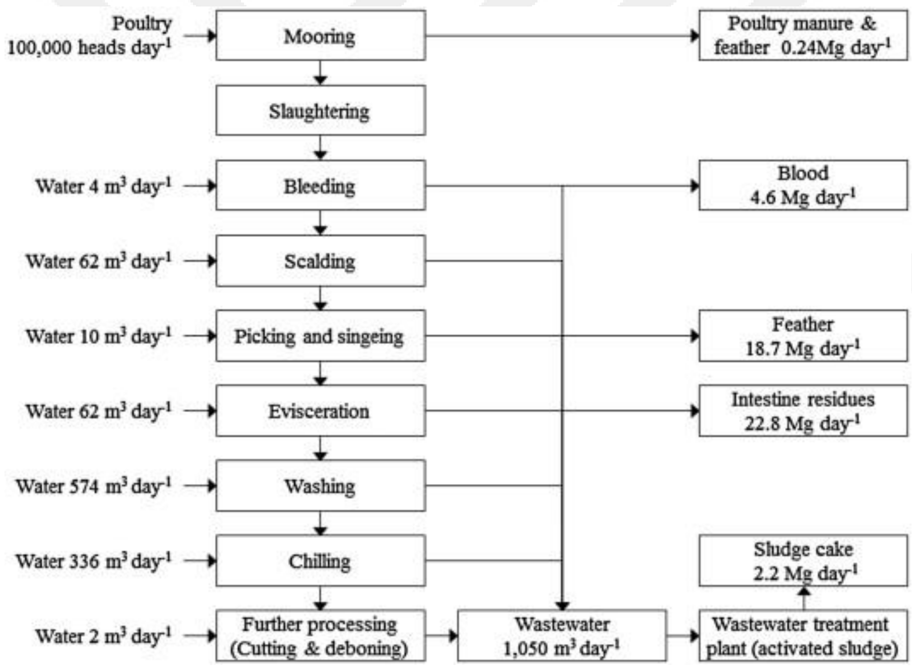

Figure 2.11. Poultry slaughterhouse wastes produced at a capacity of 100,000 heads day-1 (Yoon et al., 2016)

Another study related to poultry sludge was performed by Ruiz-Espinoza et al. (2012). The thermal pre-treatment of poultry slaughterhouse sludge for low temperatures and variable exposure times as a pre-hydrolysis technique to increase the efficiency of anaerobic digestion process was evaluated in their study. The results revealed that the most efficient conditions for solubilizing organic molecules were 90°C and 90 minutes by increasing the 10%.

3. MATERIAL METHOD

3.1. Material

3.1.1. Dewatered Poultry Sludge

Water is largely utilized in the poultry slaughtering industry for scalding during the feather removal process, bird washing before and after evisceration, sterilization of equipment and facilities. The wastewater is treated using a coagulation-flocculation process; the physicochemical sludge produced contains food waste for birds, high moisture, blood, manure, animal fats, proteins, and high amounts of pathogenic bacteria. Dewatered Poultry Sludge was chosen as feedstock for the current study considering its attractive properties such as calorific value, and high feedstock. The calorific value of DPS is higher than many biomass types and similar to coal (Llorente & García, 2008; Vassilev et al., 2015). The amount of DPS produced by the slaughterhouse can vary between 70-to-80 tonnes per day (Sittijunda et al., 2010).

A private corporation located in Adana, Turkey supplied the biomass feedstock of DPS. Then, DPS samples were dried in a conventional oven at 105 °C for 24 hours in order to adjust the moisture content, which is one of the experimental parameters, according to the parameter range (see in Figure 3.1).

Figure 3.1. Freshly collected and dried dewatered poultry sludge in a conventional furnace

Then, dried DPS samples were filled in sealed plastic containers as shown in Figure 3.2 and stored in deep-freeze to prevent biological degradation and keep the moisture content constant.

Figure 3.2. Sealed DPS in plastic containers

Meanwhile, the characterization of DPS was also performed for comparison. The calorific value (higher heating value) of DPS (26.58MJ/kg) was determined through the bomb calorimeter, and the elemental and proximate analyses were carried out according to the American Society for Testing and Materials (ASTM) standards. The mass fractions of Carbon (C), Hydrogen (H), Nitrogen (N), Sulfur (S), and Oxygen (O) were determined by the elemental analysis, whereas the proximate analysis determined the fixed carbon content, volatile matter, and ash content. These initial data were utilized for comparison with wet torrefied samples to address the effects of WT on fuel properties of DPS.

Before starting the experiments, the DPS samples were crushed into small pieces, as can be seen in figure 3.3, to increase the reaction surface area and decrease the reaction time, so that obtain more efficient results.

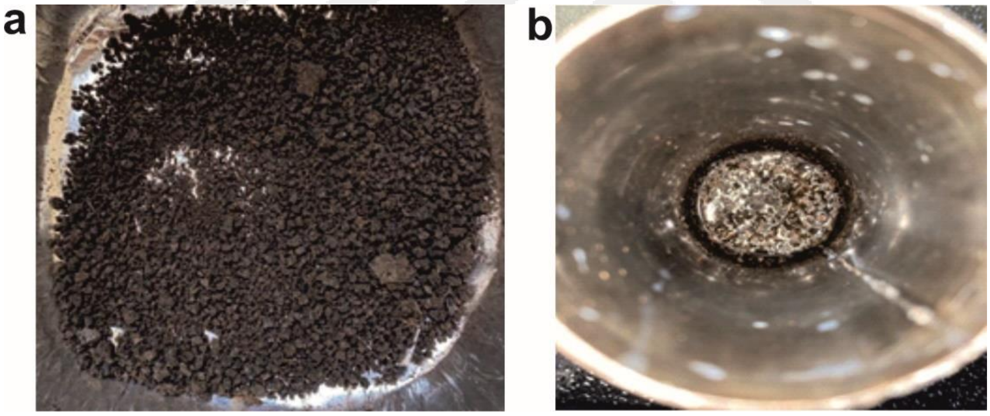

Figure 3.3. (a) Crushed DPS and (b) its mixture with water in the reactor

3.1.2. Experimental Setup

The wet torrefaction experiments were carried out in a laboratory-scale high-pressure reactor with 500 mL volume, shown in Figure 3.4 and Figure 3.5. The reactor was made from AISI 316 stainless steel as a closed autoclave, so the generated stream increases the pressure. A stirring unit was included inside the reactor having a maximum rotation rate of 350 rpm (3). Heating was provided by a

4 kW electric mantle heater (2), and a PID controller unit (8) enabled the simultaneous observation and adjustment of the reaction temperature, heating rate, pressure, and time. Two valves (4) on the reactor were used to supply nitrogen flow from a tank (1) and collection of the gaseous product.

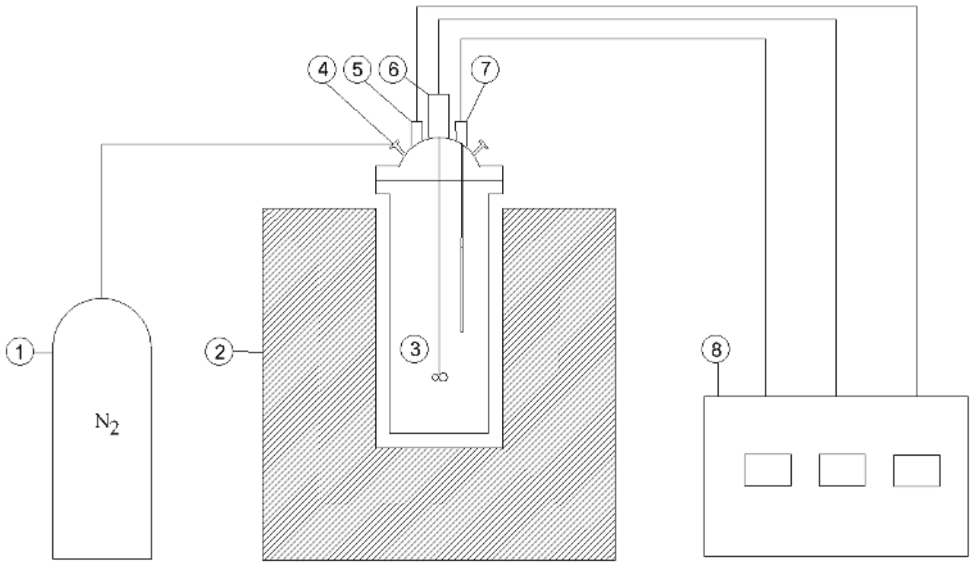

Figure 3.4. Schematic presentation of the experimental setup: 1-Nitrogen tank; 2-Electrical Heater; 3-Reactor; 4-Valves; 5-Pressure sensor; 6-Stirrer unit; 7-Thermocouple; 8-PID controller.

Figure 3.5. Experimental Setup

3.2. Method

The way that we followed in our present work is represented in Figure 3.5. Our work is started with the sample collection, then collected samples were subjected to the drying process to ensure the amount of moisture in biomass was eliminated. The drying process was followed by the initial characterization of biomass according to proximate, ultimate, and calorific value analysis. Then, operating parameters and response parameters were selected to perform the wet torrefaction experiment. After the selection of parameters, experiments were designed according to response surface design. Finally, experiments were conducted and torrefied biomasses were subjected to characterization process as before. Consequently, torrefied and raw samples' fuel characteristics were compared, and interactive effects of the operating parameters were discussed.

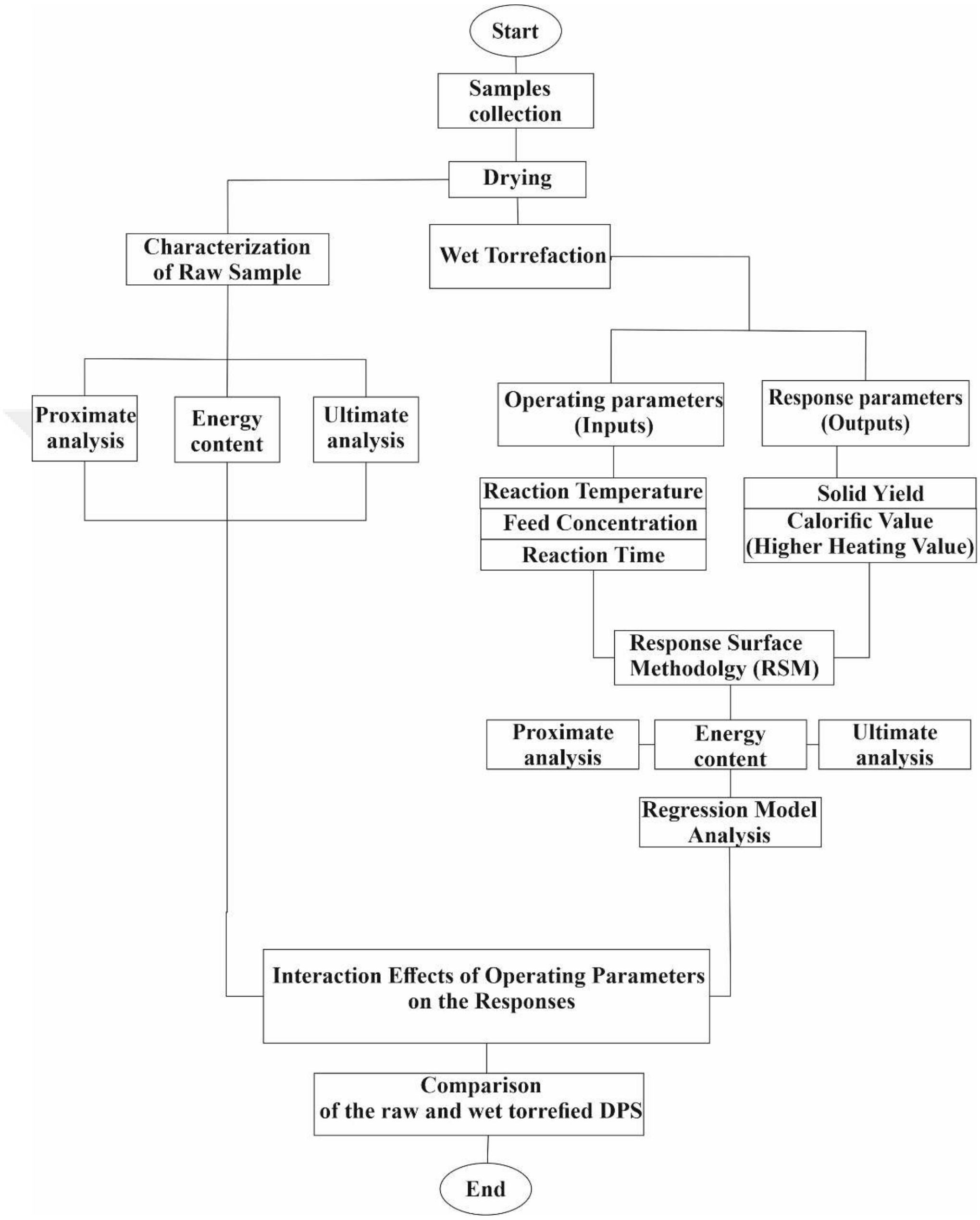

Figure 3.6. Flowchart of work

3.2.1. Response Surface Methodology

The RSM can be described as a collection of statistical and mathematical techniques that aims to optimize the responses by establishing the effects of the variables on them independently and interactively. To figure out the characteristics of the model, the RSM provides valuable information for the experiments. The data generated from RSM are then be used to generate a second-order predictive model that relates the input process parameters to the response variables. In this study, Box-Behnken Design (BBD) was utilized, which allows users to investigate three input process parameters that affect responses in less time and fewer experimental runs than other experimental designs. (Ozonoh et al., 2020).

The Box-Behnken design emphasizes the extremes generated by every two variables, as well as the domain's center point. As a result, the Box-Behnken design is a fractional factorial design that can also be regarded as a fractional central composite design. It is simple to construct: it is recommended to have multiple repeated runs at intermediate levels; two factors with upper or lower factor values while other factors are kept at intermediate levels. As a result, for an n-factor experiment, the total number of experimental runs is 2n(n-1) plus the number of runs at the center (Liu, 2020).

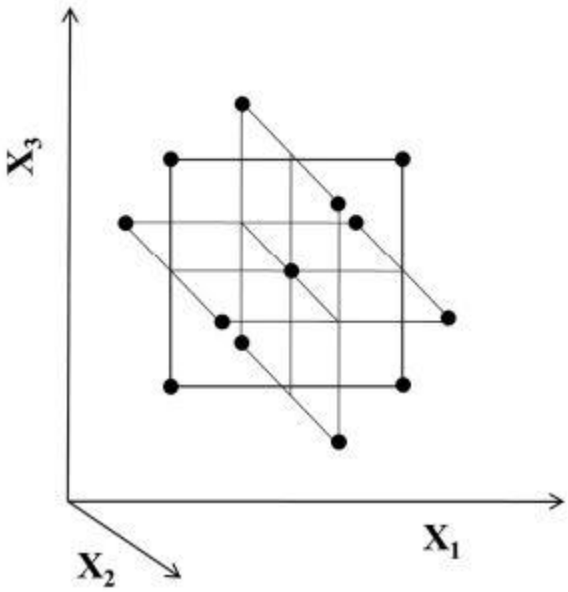

Figure 3.7. Box-Behnken design for the optimization of a three-factor system (Müller et al., 2020).

To ensure the characteristics of the model and second-order polynomial predictive model generated by the RSM, Regression analysis and Pareto analysis of variance (ANOVA) were performed using the data of experiments. Minitab was used as statistical software to generate models to estimate the calorific value (CV) of produced hydrochar and solid yield. Then, F-test was conducted to indicate the effect of each independent operation parameter. Associated p-value evaluates whether the F-value is large enough to be considered significant (Zaman et al., 2020). The model precision can also be justified by the value of correlation coefficient (R^2) and adjusted correlation coefficient (R^2_{Adj}), which vary between zero to one. The correlation coefficient close to one indicates high accuracy in the developed model. However, R^2_{Adj} does not increase with adding more independent variables to the model, contrary to R^2. Therefore, R^2_{Adj} accounts for more reliable results.

3.2.2. Wet Torrefaction Procedure

The main parameters, together with the RSM results of the study, are listed in Table 1.1. The wet torrefaction was initiated by loading the poultry sludge with distilled water into the reactor, then mixing at a predetermined concentration of (10: 30: 50) wt%. The rotation of stirring was kept constant at a rate of 100 rpm during the mixing. The required inert reaction atmosphere was satisfied by introducing nitrogen at 1 bar into the sealed reactor until the air was completely discharged. The pressure was kept within the range of sub-critical pressures auto-generated by heat supply, and its value was throughout the experiments. The reactor was kept under predetermined reaction time intervals of (20: 40: 60) min when the reaction temperatures approached the desired levels of (180: 230: 260) °C. Then, the reactor was submerged into an ice bath for cooling until the temperature dropped to room temperature. After the cooling process, the products were collected from the reactor. Hydrochar and liquid products were separated from each other with the help of a filter paper having 10μm pore size. Hydrochar is then subjected to a drying process to eliminate possible reactions during storage that lead to inaccurate results in oncoming analysis.

Table 1.1. Experimental ranges of independent process parameters and their coded levels for Box-Behnken design.

Independent Process Parameters (Input Variables)	Coded Level Factors		
	-1	0	+1
Reaction temperature (°C)	180	10	20
Biomass concentration (wt%)	230	30	40
Residence time (min)	280	50	60

3.2.3. Characterization of DPS

The products of wet torrefaction and the DPS were subjected to further measurements for comparison. Firstly, the calorific values were measured according to ASTM D 5865 standards (Standard Test Method for Gross Calorific

Value of Coal and Coke) utilizing SDACM 3100 Bomb Calorimeter (Sundy Science and Technology Co., Ltd. 2017). Then, ultimate (or elemental) analysis was performed according to ASTM 3176 (Standard Method for Ultimate Analysis of Coal and Coke) using an elemental analyzer (Flash 2000 CHNS by Thermo Scientific™). The next step of measurements was involved with proximate analysis (thermogravimetric analysis), which was performed using a thermogravimetric analyzer (TGA/DSC 3+ by Mettler Toledo) based on ASTM E 1131 (Standard Test Method for Compositional Analysis by Thermogravimetry).

Finally, a series of calculations and analyses were performed to reveal the differences in fuel properties of DPS and hydrochar. The solid yield was determined using equation (3.1) to see the effectiveness of wet torrefaction on the products.

$$SY_{Experimental}\,(\%) = \frac{Mass\ of\ Hydrochar}{Mass\ of\ Poultry\ Sludge} \times 100\% \tag{3.1}$$

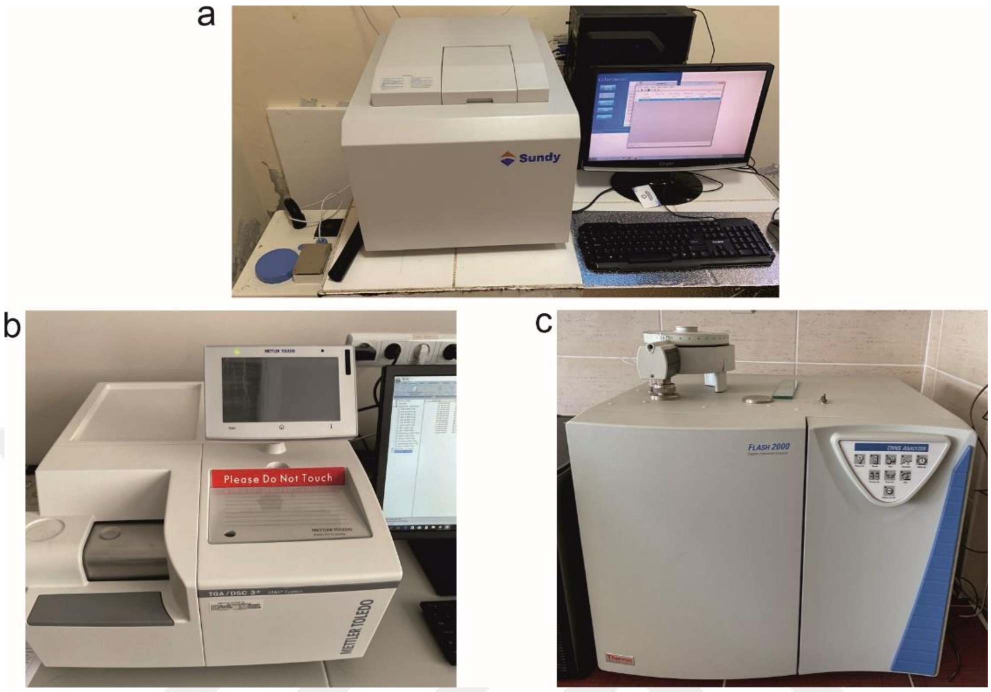

Figure 3.8. (a) SDACM 3100 Bomb Calorimeter, (b) TGA/DSC 3+ by Mettler Toledo, (c) Flash 2000 CHNS by Thermo Scientific™

4. RESULTS AND DISCUSSION

4.1. The Results of Response Surface Model

The obtained results from RSM applied to the experimental data are listed in Table 4.1, where X_1, X_2, and X_3 represent the temperature, feed concentration, and reaction time, respectively. It can be stated that the model is statistically significant since the p-value of the model is less than 0.05. The p-value of the lack-of-fit is higher than 0.05; hence the data match well with the model. Besides, the values of R^2 and R^2_{Adj} are calculated as 0.9798 and 0.9435, respectively, which satisfies high quality in the predicted model.

Table 4.1. Model Coefficients and ANOVA of Calorific Value

Source	Degree of Freedom	Sum Of Square	Mean Of Square	F-Value	P-Value	
Model	9	5.26836	0.58537	30.84	0.001	**Significant**
Linear	3	4.81914	1.60638	84.63	0.000	
X_1	1	2.10843	2.10843	111.08	0.000	
X_2	1	2.19661	2.19661	115.73	0.000	
X_3	1	0.51410	0.51410	27.09	0.003	
Square	3	0.08745	0.02915	1.54	0.314	
X_1^2	1	0.00603	0.00603	0.32	0.597	
X_2^2	1	0.00917	0.00917	0.48	0.518	
X_3^2	1	0.07091	0.07091	3.74	0.111	
2-Way Interaction	3	0.36177	0.12059	6.35	0.037	
X_1X_2	1	0.17264	0.17264	9.10	0.030	
X_1X_3	1	0.06275	0.06275	3.31	0.129	
X_2X_3	1	0.12638	0.12638	6.66	0.049	
Error	5	0.09490	0.01898			
Lack-of-Fit	3	0.04458	0.01486	0.59	0.678	**Insignificant**
Pure Error	2	0.05033	0.02516			
Total	14	5.36326				
R^2=98.23%, R^2_{Adj}=95.05%						

The CV of regression model for the torrefied DPS (TDPS) was determined using the following equation (4.1).

$$CV = 25.04 + 0.0016X_1 - 0{,}0319X_2 + 0{,}0559X_3 + 0{,}000016X_1^2 - 0{,}000125X_2^2 - 0{,}000346X_3^2 + 0{,}000208X_1X_2 - 0{,}000125X_1X_3 + 0{,}000444X_2X_3 \quad (4.1)$$

Table 4.2 presents the ANOVA of solid yield (SY) calculated using equation (4.2). The p-value of the model in the ANOVA of the SY is below 0.05, so the model is determined to be statistically significant. Furthermore, the data fit the model well since the p-value of lack-of-fit is higher than 0.05. The correlation coefficients, R_2 and R_{2Adj} are 0.9737 and 0.9265, respectively, providing enough quality in the predicted model. SY after WT is shown in Figure 4.1.

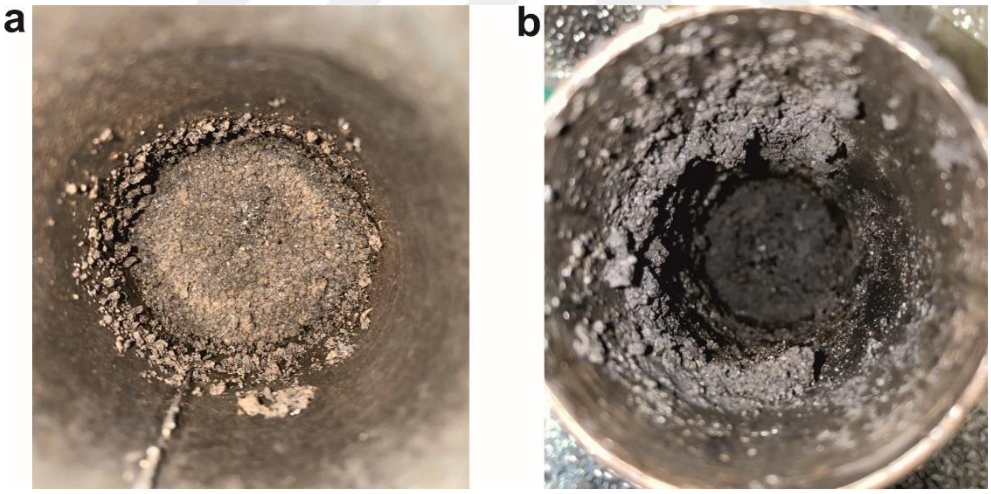

Figure 4.1. (a) DPS before implementing WT, (b) SY after implementing WT.

Table 4.2. Model Coefficients and ANOVA of Solid Yield

Source	Degree Of Freedom	Sum Of Square	Mean Of Square	F-Value	P-Value	
Model	9	483.762	53.751	51.56	0.000	**Significant**
Linear	3	459.529	153.176	146.94	0.000	
X_1	1	174.570	174.570	167.46	0.000	
X_2	1	266.137	266.137	255.29	0.000	
X_3	1	18.822	18.822	18.05	0.008	
Square	3	8.990	2.997	2.87	0.143	
X_1^2	1	0.257	0.257	0.25	0.641	
X_2^2	1	3.208	3.208	3.08	0.140	
X_3^2	1	5.736	5.736	5.50	0.066	
2-Way Interaction	3	15.242	5.081	4.87	0.060	
X_1X_2	1	9.412	9.412	9.03	0.030	
X_1X_3	1	5.469	5.469	5.25	0.071	
X_2X_3	1	0.362	0.362	0.35	0.581	
Error	5	5.212	1.042			
Lack-of-Fit	3	3.852	1.284	1.89	0.365	**Insignificant**
Pure Error	2	1.360	0.680			
Total	14	488.974				
R^2=98.93%, R^2_{Adj}=97.02%						

The determined regression model equation for the SY of TDPS in the coded parameters was calculated by:

$$SY_{regression} = 118.3 + 0.235X_1 - 0.045X_2 + 0.119X_3 + 0.000106X_1^2 - 0.00233X_2^2 - 0{,}00312X_3^2 + 0.001534X_1X_2 - 0.001169X_1X_3 + 0.0075X_2X_3 \quad (4.2)$$

The calorific value and solid yield were calculated according to equations 4.1 and 4.2. The scatter plots of calculated SY and CV with experimental data are presented in Figure 4.2 for comparison. It can be concluded that the developed regression model equations are well-fitted since the experimental values of CV and SY are close to the regression line.

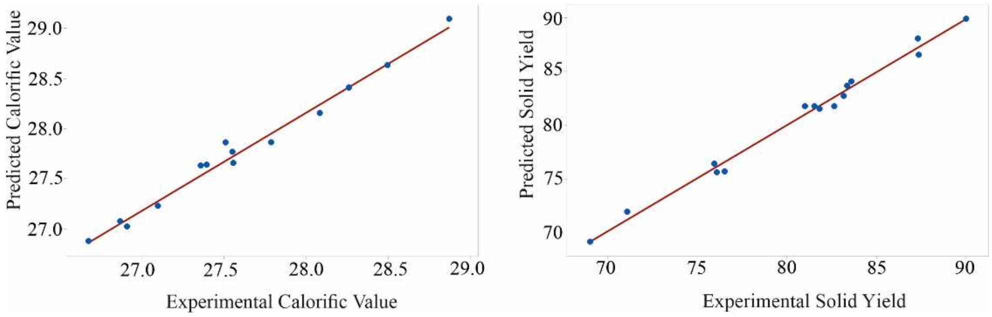

Figure 4.2. Predicted and Actual values of CV and SY

Each parameter has distinctive effects on the calorific value (CV) and solid yield (SY) of TDPS. Using the Pareto Charts, significant terms can be determined with the help of a reference line. The reference line indicates the statistically significant parameter, having an α value of 0.05, corresponding to a confidence level of 95% (see Figures 4.3). It can be observed that the feed concentration is the most effective operating parameter on the CV and SY, followed by the reaction temperature. The least effective parameter is, therefore, the reaction time. In terms of CV, similar effects of feed concentration were reported by Volpe and Fiori (2017). In their study, the range of feed concentration was varied from 7%wt to 25%wt at the same temperature of 250 °C and it was found that an increase in feed concentration enhance the calorific value. Considering the effect of feed concentration on SY quite consistent with the study of Murillo et al (2022), higher feed concentration originates earlier polymerization of biomass hence higher SY can be obtained (Funke et al., 2010). The effect of reaction temperature and time on both CV and SY can be explained by reaction kinetics. The first-order rate law for a thermal decomposition reaction can be expressed as:

$$d\alpha/dt = k[\mathrm{T}]\, f(\alpha) \quad (4.3)$$

where α is the conversion degree, $f(\alpha)$ is a function of conversion degree, and k is the rate constant defined according to Arrhenius equation as follow:

$$k[\mathrm{T}] = \mathrm{A}\exp\left(-\frac{E_{\alpha}}{RT}\right) \qquad (4.4)$$

where A is the pre-exponential factor, E_{α} is activation energy and R is gas constant. As equations 4.3 and 4.4 indicates that the reaction time is directly proportional to reaction rate, however, the reaction temperature is exponentially proportional to reaction rate. Therefore, the effect of reaction time is lower on CV and SY when compared to temperature.

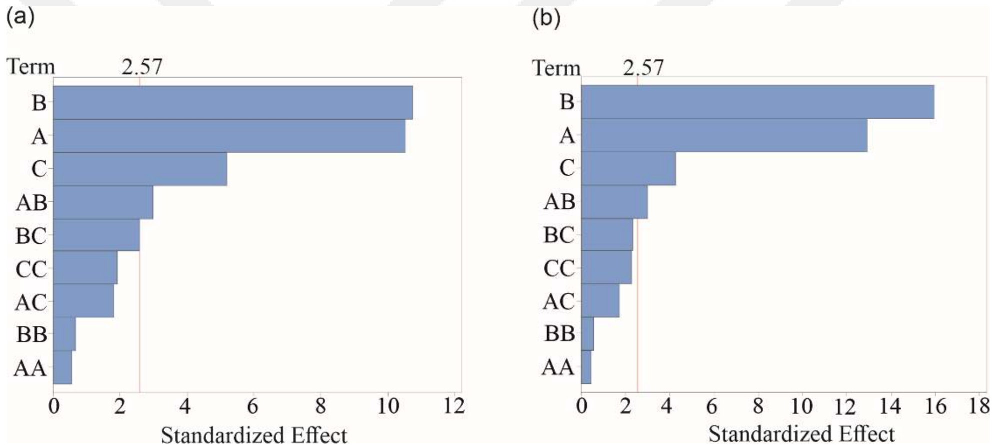

Figure 4.3. Pareto Chart of the Standardized Effects on (a) Calorific Value and (b) Solid Yield, where A is Reaction Temperature, B is Feed Concentration, C is Reaction Time

According to Desirability of the Composite (Optimum Condition), maximum CV and SY were evaluated to be 0.8390, 0.9793, and 0.7189, respectively (see Figure 4.4). The red line in the columns represents the level of independent process parameters that provides a maximum level of responses. As can be seen from the first and third columns maximum calorific value together with solid yield do not require the highest level of independent process parameter whereas the second column indicates that the highest level of feed concentration is necessary to obtain optimum conditions.

A summary of experiments performed is listed in Table 4.3 with corresponding calorific values and solid yield responses. It is observed that the highest CV (28.87 MJ/kg) is obtained under conditions of 280 °C, 50wt%, and 40min. On the other hand, the highest SY is obtained at 180°C, 50wt%, and 40min. Since the goal is to attain the maximum CV and SY for wet TDPS, optimum conditions predicted by RSM were given as 268°C, 50wt%, and 47min, which provide CV and SY of 28.64MJ/kg and 85.2wt%, respectively. Hence, the wet torrefaction increased the CV of DPS by 7.75% at optimum conditions.

The response values predicted at optimum conditions and experimentally obtained response values were summarized in Table 4.3. Considering the data, errors between predicted and experimental for CV and SY were calculated to be 0.62% and 1.12%, respectively.

Table 4. 3. Predicted and Experimental Response Values of Optimum Conditions

	A (℃)	B (wt%)	C (min)	Predicted Responses		Experimental Responses	
				CV (MJ/kg)	SY (%)	CV (MJ/kg)	SY (%)
Optimum Coditions	268	50	47	28.82	84.07	28.64	85.20

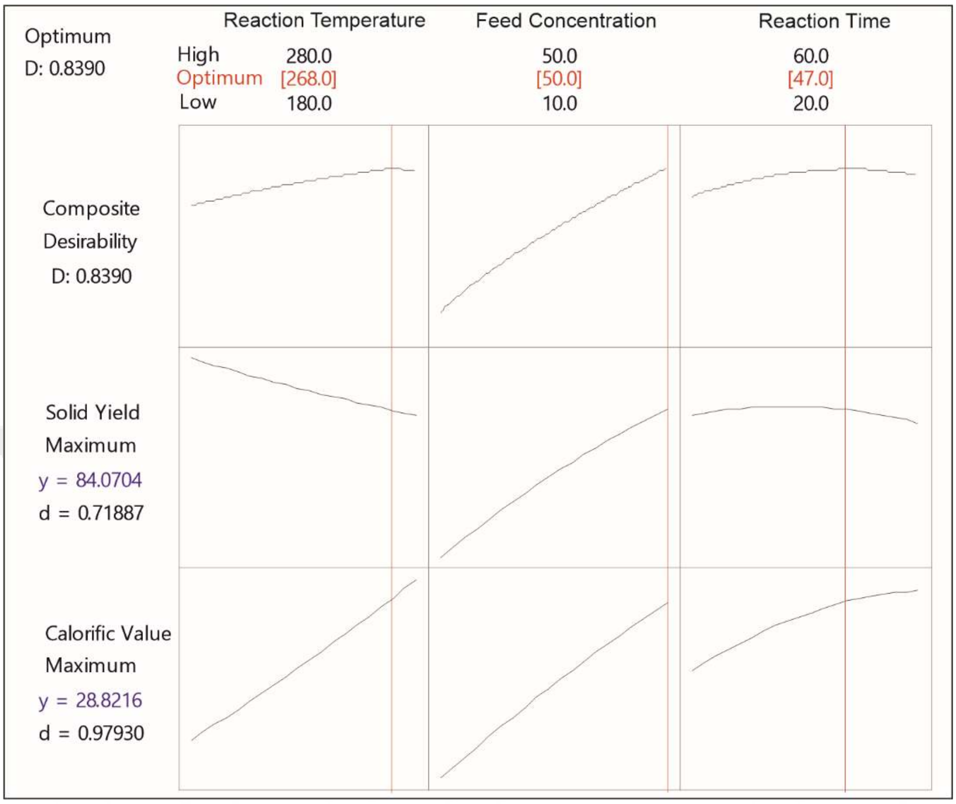

Figure 4. 4. Optimization of Responses with Desirability levels

Table 4.4. Experimental design matrix, Calorific Value, and Solid Yield responses

Run	Reaction Temperature (℃)	Feed Concentration (wt%)	Reaction Time (min)	Calorific Value (MJ/kg)	Solid Yied (%)
1	230	50	60	28.49	83.5568
2	180	30	60	27.36	83.1496
3	230	30	40	27.51	82.5994
4	280	30	20	28.08	75.9333
5	280	30	60	28.26	76.5064
6	230	30	40	27.78	80.9868
7	180	30	20	26.68	87.2536
8	230	10	20	26.87	76.0747
9	230	10	60	27.10	71.1030
10	230	30	40	27.78	81.4939
11	180	10	40	26.91	81.8012
12	180	50	40	27.55	89.9524
13	280	50	40	28.87	83.3167
14	230	50	20	27.55	87.3250
15	280	10	40	27.30	69.0298
Optimum Conditions	268	50	47	28.64	85.2

4.2. Interaction Effects of Operating Parameters on the Calorific Value and Solid Yield

In this section, three-dimensional surface plots were utilized to present the effect of wet torrefaction on DPS's product responses (CV and SY). In addition, two-dimensional contour plots were also included for each case to interpret the results more quantitatively. Since it was impossible to represent all three parameters' effect on responses by either a single contour or three-dimensional plot, one of the parameters was maintained at the optimum level with varying two parameters.

4.2.1. Feed Concentration and Reaction Temperature

The change in feed concentration and reaction temperature at the optimum reaction time of 47 min significantly affects both CV and SY, as shown in Figure 4.5. As mentioned previously by the RSM results, the feed concentration and reaction temperature are considered the most influential parameters on the CV. It can be observed from Figure 4.5 (a) that the CV sharply rises with increasing feed concentration and reaction temperature, in agreement with the studies of Erses Yay et al. (2021), Volpe and Fiori (2017), and Aragon- Briceno et al. (2020). In comparison with Figures 4.6 and 4.7, there is a more linear surface in Figure 4.5 since quadratic terms (X_1^2, X_2^2, X_1X_2) have less impact on CV and SY. Figure 4.5 (b) shows that increasing the feed concentration provides better SY while the temperature has a detractive effect. In Figure 4.5 (a), distances between contours cumulatively decrease it implying that the effect of parameters is more impactful at higher levels. On the other hand, it can be observed in figure 4.5 (b) that the contours are getting further and further away from each other since temperature and feed concentration have an opposite effect to each other on SY, in correspondence with the study of Singh et al. (2020).

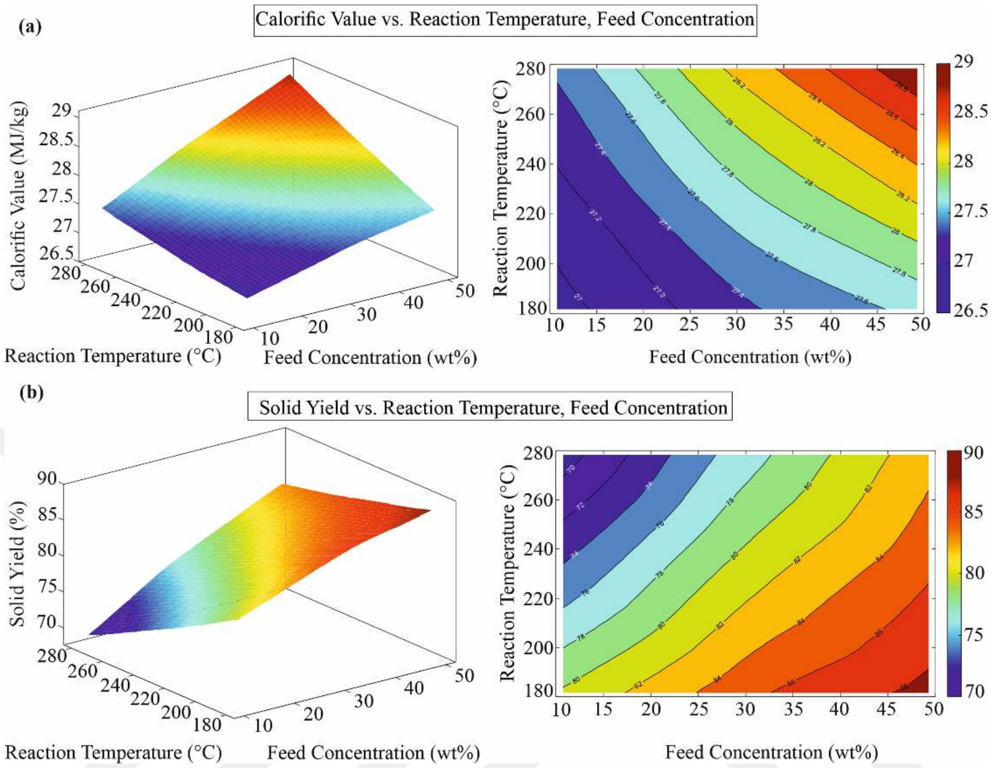

Figure 4.5. The effect of reaction temperature and feed concentration on calorific value, CV (a) and solid yield, SY (b)

4.2.2. Reaction Temperature and Reaction Time

It is reported from previous studies that the CV of torrefied DPS (TDPS) increases with increasing reaction temperature and time, whereas SY decreases (Bach et al., 2014; Zhang et al., 2016; Zhang et al., 2017). Similarly, an increase in CV is observed in Figure 4.6 (a) with increasing operating parameters at the optimum feed concentration of 50wt%. Compared to Figure 4.5, the impact of the quadratic terms (X_2^2, X_3^2, X_2X_3) is more noticeable in Figure 4.6, especially in 4.6 (b). In Figure 4.6 (a), CV significantly increased with increasing reaction time from 20 to 40min while the reaction temperature maintains the positive effect on CV in a linear trend. It can be observed that the effectiveness of temperature is higher than time since contours are shaped horizontally rather than diagonal or vertical in

Figure 4.6 (a) in correspondence with the investigation of Makela et al. (2015), who reported that the effect of reaction time on the CV and SY is 3-to-7 times less compared to reaction temperature. As can be seen from figure 4.6 (b) contours become diagonal after 40 min it indicating that the influence of the time on SY is more prominent between 40-60 min.

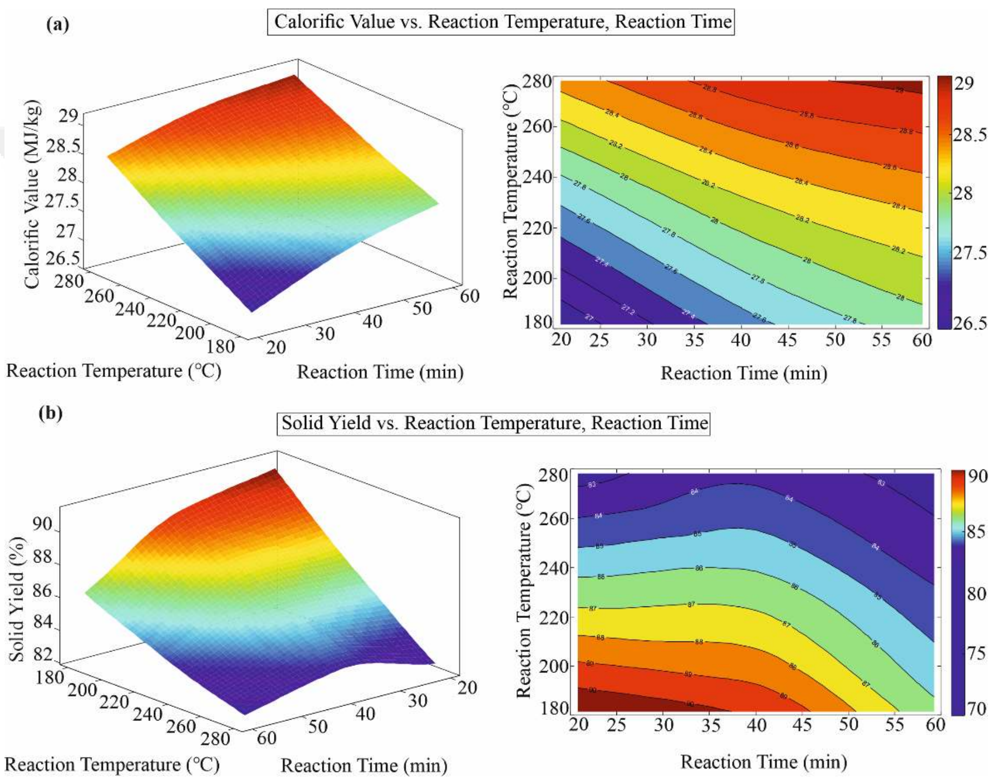

Figure 4.6. The effect of reaction temperature and time on calorific value, CV (a) and solid yield, SY (b)

4.2.3. Reaction Time and Feed Concentration

The effect of reaction time and feed concentration on the responses is presented in Figure 4.7. Although the reaction time does not affect the CV as much as feed concentration, it was evaluated that the increasing reaction time has a positive effect on the CV. Similar to Figure 4.6 (a), while the effect of reaction time is evident between 20-40 min in 4.7 (a), the most effective parameter, the feed concentration, is dominant at all levels. The dominant effect of the feed concentration can be seen most clearly in figure 4.7 (b) since the contours take an almost strictly vertical shape. On the other side, the reaction time has an inverse effect on the SY.Reaction time gradually reduces the value of SY, in contrast, to feed concentration. It should be noted that the evaluated results are in agreement with the studies of Chen et al. (2012), Bach et al. (2017), and Singh et al. (2019).

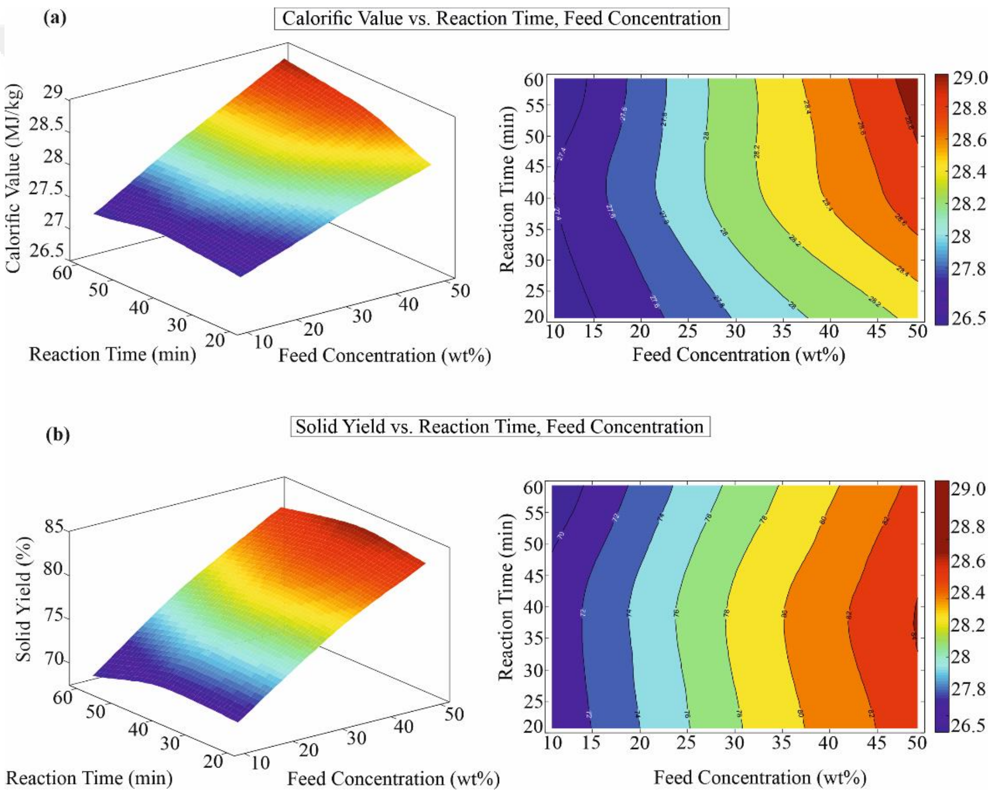

Figure 4.7. The effect of reaction time and feed concentration on calorific value, CV (a) and solid yield, SY (b)

4.3. Results of Proximate and Ultimate Analysis

The results of Proximate analysis (Thermogravimetric analysis) are presented in Figure 4.7 and Table 4.4. After providing the sample in the device, the experiment was carried out by starting at room temperature and gradually increasing the temperature up to 105°C, at a rate of 10°C/min heating rate with 40ml/min nitrogen flushing. At T=105°C, an isothermal process was employed by keeping the temperature constant for 15 min. Then the temperature was increased up to reach 600°C, at a rate of 20°C/min heating rate. Later, another isothermal process was employed at 600°C for 5 min during which the nitrogen flow was turned off and replaced with the oxygen flow at the same temperature. The last step of the proximate analysis was involved with an increase in temperature 600°C to 1000°C at 20°C/min. Finally, the TGA instrument was naturally cooled down to room temperature.

Better solid fuel properties can be observed at TDPS268-50-47 in Table 4.5, which is regarded as optimum condition according to RSM and the experiments; i.e., the amount of ash content is reduced from 25,09 to 22,18 wt%, whereas the amount of fixed carbon is increased from 7,41 to 10.70 wt%, and volatile matter (VM) decreases slightly. On the other hand, the proximate analysis results of the TDPS280-50-40 experiment where the highest caloric value is obtained show better solid fuel properties than the (Table 4.5) DPS. These outcomes from the proximate analysis are in agreement with Indrawan et al. (2012) and Lin et al. (2017). The amount of VM is high, and it can be observed that the changes can be neglected for all conditions. Since high volatile matter increases DPS reactivity, improves the thermal process, and decreases the ignition temperature (Saffe et al., 2019), keeping its value at high levels after the torrefaction can be considered another advantage biomass considered in this study. Figure 4.8. shows the TGA curves, representing the thermal behavior of the DPS and TDPS in the temperature range of 25–1000°C.

Table 4.5. Proximate Analysis of raw and TDPS (dry basis)

Sample	Proximate Analysis[2]		
	VM	FC	Ash
Raw DPS	67.50	7.41	25.09
TPDS267[1]-50[2]-47[3]	65.97	11.05	22.97
TDPS280-50-40	66.11	11.70	22.18

VM= volatile matter, FC= fixed carbon,[1]=°C, [2]=wt%, [3]=min

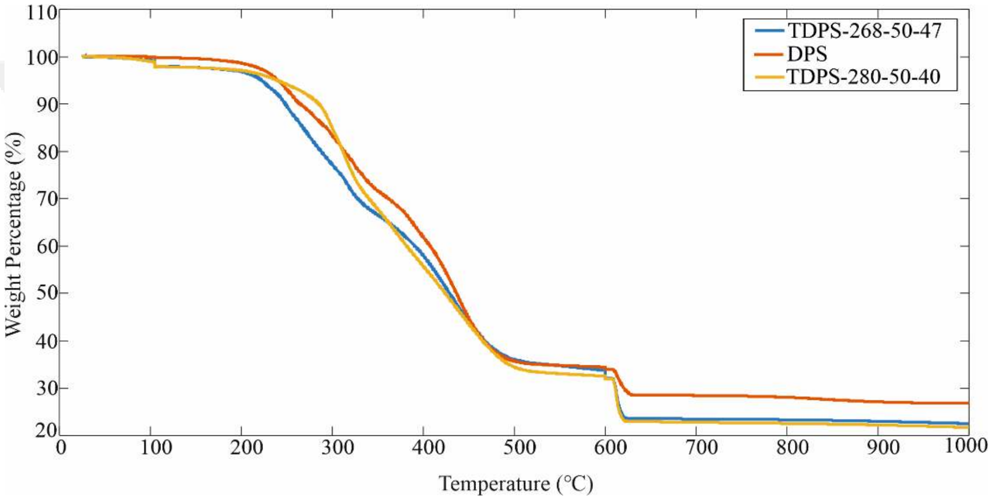

Figure 4.8. Thermogravimetric (TGA) curves for combustion of raw and TDPS

It is observed that the ratio of *O/C* decreases illustrated in Figure 4.9.; however, there is a slight increase in the *H/C* ratio since the main gas product of the wet torrefaction process is carbon dioxide (CO_2) which agrees well with the studies of Alam et al. (2021) and Ma et al. (2021). The decrease in the O/C ratio can be explained by decarboxylation reactions and detected by the Fourier Transform Infrared spectroscopy (FTIR) analysis (Funke et al., 2010). A series of hydrothermal carbonization experiments have been conducted by Li et al. (2021) according to their FTIR results, a decrease in C=O groups indicates decarboxylation on the surface of hydrochars.

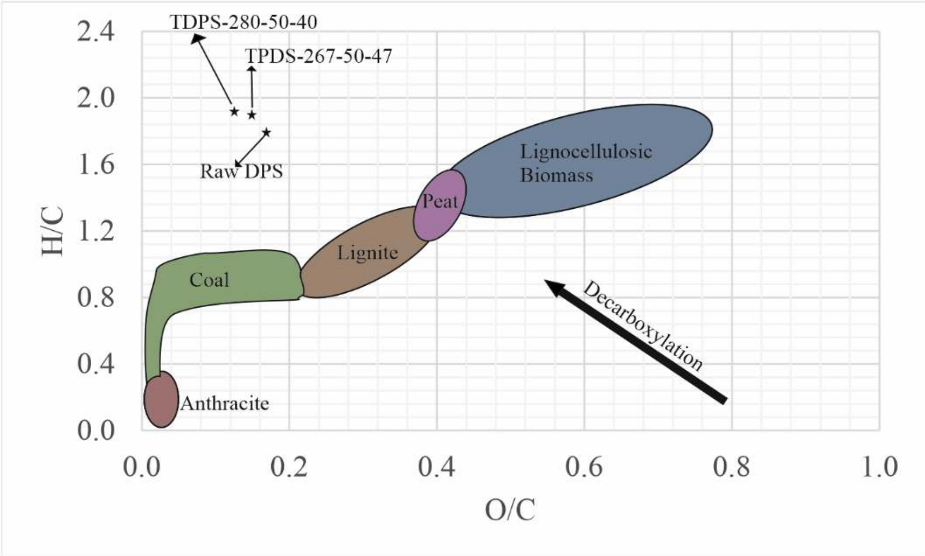

Figure 4. 9. Van Krevelen diagram for raw and wet torrefied DPS

Considering the ultimate, proximate, and calorific value analysis it can be concluded that the fuel properties of TDPS are enhanced, and it could be considered a more efficient sample for subsequent conversion methods such as gasification or pyrolysis (Chew et al., 2020; Olszewski et al., 2020) Moreover, the increase in carbon content and the decrease in oxygen and ash can transform the TDPS into a coal-like structure (Volpe and Fiori, 2017), another promising result of the current study.

Table 4. 6. Ultimate Analysis of raw and TDPS (dry basis)

Ultimate Analysis[1]					O/C[3]	H/C[3]
C	H	N	S	O[2]		
51.13	7.67	4.24	0.34	11.53	0.169	1.78
53.43	8.17	3.67	0.52	11.24	0.158	1.86
55.43	8.78	3.03	0.49	10.09	0.136	1.89

[1]=wt%, [2]= calculated by difference, [3]= atomic ratio

5. CONCLUSION

This study was performed to investigate the effects of reaction temperature, time, and feed concentration on the calorific value and solid yield of torrefied dewatered poultry sludge (TDPS) obtained from wet torrefaction (WT). Response surface methodology was utilized to design experiments and identify the parameters. Then, experiments in a laboratory-scale high-pressure reactor were conducted, followed by proximate and ultimate analysis. The results revealed that reaction temperature, time, and feed concentration remarkably affect the calorific value (CV) and solid yield (SY) of TDPS. Despite the effects of reaction temperature and time, the effect of feed concentration on CV and SY was determined to be the most dominant. Furthermore, the interaction effects of process parameters were observed. It was obtained that all interactive effects of parameters enhance the CV of DPS. However, reaction temperature and time were found to decrease the SY. Therefore, the interactive effect of reaction temperature and time with the feed concentration presented adverse effects on SY.

In order to optimize the responses aiming the maximum CV together with maximum SY, temperature, feed concentration, and reaction time were evaluated by RSM to be 268 °C, 50wt%, and 47 min, respectively. Moreover, TDPS was subjected to characterization analyses: Ultimate analysis results showed that the oxygen to carbon ratio, O/C of TDPS decreases by 6.5% (from 0.169 to 0.158), compared to DPS at optimum conditions. Furthermore, the proximate analysis demonstrated a significantly reduced ash content (from 25.09% to 22.97%) with an increased fixed carbon (from 7.41% to 11.05%), together with a slightly less volatile matter. Lower O/C, ash content, volatile matter, and higher fixed carbon can be considered indicators of an upgraded DPS, hence a more efficient sample. Therefore, it can be concluded that WT provides better solid fuel properties when applied to DPS, and it needs to be applied for other biomass samples due to its high potential for enhanced fuel characteristics.

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