RESEARCH ARTICLE ISSN 2730-2334 (Online)

กระบวนการไพโรไลซิสเชิงตัวเร่งของน้ำมันพืชใช้แล้วไปเป็นน้ำมันเชื้อเพลิงชีวภาพสำหรับเครื่องบินในเครื่องปฏิกรณ์แบบสกูรต่อเนื่อง

PRODUCTION OF ALTERNATIVE AVIATION BIOFUELS FROM CATALYTIC PYROLYSIS OF WASTE VEGETABLE OIL IN A PILOT-SCALE CONTINUOUS SCREW PYROLYZER

นันทนา ลามาตย์ สแลตเตอร์[1]*, บุญวัฒน์ วิจารณ์พล*[1]*, ธราพงษ์ วิทิตศานต์*[2]****

Nantana Lamart Slatter[1]*, Bunyawat Vichanpol*[1]*, Tharapong Vitidsant*[2]****

[1]*ภาควิชาพลังงานทดแทน วิทยาลัยพลังงานและสิ่งแวดล้อม มหาวิทยาลัยพะเยา*

[1]*Renewable Energy Department, School of Energy and Environment, University of Phayao.*

[2]*ภาควิชาเคมีเทคนิค คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย*

[2]*Department of Chemical Technology, Faculty of Science, Chulalongkorn University.*

**Corresponding author, e-mail: Tharapong.V@Chula.ac.th*

Received: *2 March 2023;* ***Revised:*** *10 April 2023;* ***Accepted:*** *2 May 2023*

บทคัดย่อ

งานวิจัยนี้มุ่งเน้นศึกษากระบวนการไพโรไลซิสเชิงตัวเร่งในการเปลี่ยนของเสียน้ำมันพืชและไขสัตว์บนเครื่องปฏิกรณ์แบบสกูรต่อเนื่องเพื่อให้ได้น้ำมันเชื้อเพลิงชีวภาพสำหรับเครื่องบิน ของเสียจากน้ำมันปาล์ม น้ำมันพืชใช้แล้ว และไขสัตว์ ซึ่งประกอบด้วยกรดไขมันที่สามารถแปรสภาพทางเคมีความร้อนบนตัวเร่งปฏิกิริยาโดโลไมต์ ในงานวิจัยนี้แบ่งการดำเนินการเป็น 2 ส่วน ได้แก่ 1) การทดลองในเครื่องปฏิกรณ์ระดับห้องปฏิบัติการเพื่อหาภาวะดำเนินการที่เหมาะสมของการใช้เศษน้ำมันปาล์ม อุณหภูมิ และร้อยละโดยน้ำหนักของตัวเร่งปฏิกิริยา พบว่าภาวะดำเนินการที่เหมาะสม คือ อุณหภูมิ 425 องศาเซลเซียส เมื่อใช้ตัวเร่งปฏิกิริยาโดโลไมต์ร้อยละ 3 โดยน้ำหนัก ให้ร้อยละผลได้ของน้ำมันของเหลว ของแข็ง และแก๊สไม่ควบแน่น ร้อยละ 62.22 3.43 และ 28.50 โดยน้ำหนัก เมื่อวิเคราะห์องค์ประกอบตามคาบจุดเดือดของน้ำมันไพโรไลซิสให้ร้อยละผลได้เป็นแนฟทา เคโรซีน ดีเซล และกากน้ำมัน ร้อยละ 14.70 23.72 51.24 และ 10.32 ตามลำดับ 2) เป็นการศึกษากระบวนการไพโรไลซิสเชิงตัวเร่งจากของเสียในกระบวนการผลิตน้ำมันปาล์ม น้ำมันพืชใช้แล้ว และไขสัตว์ บนเครื่องปฏิกรณ์ขยายส่วนแบบสกูรต่อเนื่องที่มีกำลังการผลิต 800 กิโลกรัมต่อวัน โดยใช้ภาวะดำเนินการจากการทดลองในตอนที่หนึ่ง พบว่าให้ร้อยละผลได้เป็นน้ำมันของเหลว ของแข็ง และแก๊ส 66.58, 8.08 และ 25.34 โดยน้ำหนักตามลำดับ เมื่อวิเคราะห์องค์ประกอบตามคาบจุดเดือดให้ร้อยละผลได้เป็นแนฟทา เคโรซีน ดีเซล และกากน้ำมัน ร้อยละ 21.63 23.57 48.22 และ 5.58 ตามลำดับ เมื่อเปรียบเทียบการใช้ของเสียน้ำมันพืชและไขสัตว์ในเครื่องปฏิกรณ์ขยายส่วนแบบสกูรต่อเนื่องให้ร้อยละผลได้ของน้ำมันของเหลวอยู่ระหว่างร้อยละ 61 ถึง 69 โดยน้ำหนัก ซึ่งประกอบด้วยสัดส่วนของเคโรซีนอยู่ระหว่างร้อยละ 21.95 ถึง 23.90 โดยน้ำหนัก เมื่อประมาณการความคุ้มค่าในการผลิตเชื้อเพลิงสำหรับเครื่องบินที่กำลังการผลิต 800 กิโลกรัมต่อวัน มีต้นทุนการผลิตอยู่ที่ 34.5 บาทต่อกิโลกรัม ในขณะที่ราคาขายน้ำมันเชื้อเพลิงเครื่องบินที่ผลิตจากกระบวนการไฮโดรแครกกิงมีราคา

133 บาทต่อกิโลกรัม จึงมีความเป็นไปได้ที่จะนำของเสียจากน้ำมันพืชหรือไขสัตว์มาผลิตเป็นน้ำมันเชื้อเพลิงชีวภาพสำหรับเครื่องบินที่มีความคุ้มค่าและยั่งยืน

คำสำคัญ: กระบวนการไพโรไลซิสเชิงตัวเร่ง; โดโลไมต์; ของเสียจากน้ำมันพืช; ดีเซล; น้ำมันชีวภาพสำหรับเครื่องบิน

Abstract

This research aims to produce aviation biofuel using waste from vegetable oil and animal fat by catalytic pyrolysis in a continuous pilot screw reactor. The raw materials used were waste from palm oil, used cooking oil and animal fat, which were generally composed of fatty acids and converted to products by calcined dolomite as the catalyst. The research work was divided into two parts. The 1st part was the experiment in a bench reactor to determine the optimum conditions for use of waste palm oil and its reaction temperature and catalyst loading. The results of this part showed the optimum reaction temperature and catalyst loading as 425 °C and 3 wt%, respectively. The product yields of liquid, solid and gas were 68.22, 3.43 and 28.50 wt%, respectively, whereas the composition in liquid was naphtha 14.70 wt%, kerosene 23.72 wt%, diesel 51.24 wt%, and residue 10.32 wt%. The 2nd part was the production of liquid fuel from the raw material mentioned above in a pilot screw reactor with a waste palm oil feed rate of 800 kg/d. The optimum temperature, 425°C and 3 wt% catalyst loading from the 1st part, were set up to operate the pilot reactor. The liquid, solid and gas yields of this operation using waste palm oil were 66.58, 8.08 and 25.34 wt%, respectively. The composition of the liquid product was consisted of naphtha 21.63 wt%, kerosene 23.57 wt%, diesel 48.22 wt%, and residue 5.58 wt%. The experimental results of 3 types of raw material in the pilot reactor gave a product yield range of 61-69 wt%. The composition in liquid biofuel was composed of naphtha, kerosene, diesel and fuel oil, in which kerosene proportion approximately of 21.95 to 23.90%. The estimated cost per kg of kerosene (aviation biofuel) for the production of 800 kg/d, including operating and investment costs, was 34.75 baht/kg, and the actual selling price of sustainable aviation fuel (SAF) from hydrocracking process is 133 baht/kg. The advantage of this process is lower cost production than the FT synthesis process and hydrocracking.

Keywords: Catalytic Pyrolysis; Dolomite; Waste Palm Oil; Diesel; Aviation Biofuels

Introduction

Waste oils such as waste cooking oil are inexpensive and are abundant sources of carbon. It is estimated that approximately 74 million liters of waste cooking oil and 0.25 million tons of waste palm oil will be produced globally in 2020 in Thailand. However, the direct use of waste oils as fuels is not appropriate due to undesirable properties such as high viscosity, low volatility and high acidity, which can cause coking and carbon deposition in the injector or engine corrosion [1]. Transesterification of waste oil with methanol has been popularly commercialized to solve these problems, but this process creates undesired byproducts of glycerin and wastewater.

Several interesting techniques is pyrolysis or thermal cracking by breaking chemical bonds without oxygen conditions, which has been studied as the most promising waste disposal technology and the best energy recovery method due to its feedstock flexibility, nonrestrictive conditions, high conversion efficiency,

limited environmental impact, and compatibility with available engines and fuel standards [2]. Catalytic pyrolysis can further improve selectivity and pyrolysis oil properties by removing oxygenated compounds, decreasing acidity and limiting product distribution [3]. In addition, the proper catalyst enhances certain desirable reactions, such as dehydrogenation, decarboxylation and cracking, directing the reaction pathway and facilitating the desired compounds [4].

The effect of various parameters, such as temperature, heating rate, residence time, type of catalyst and catalyst loading, and inert gas sweeping rate, was explored to optimize the target products [5,6] found that 15 °C/min^{-} was the optimum heating rate for the pyrolysis of waste cooking oil. The presence of metal-based catalysts can significantly reduce the acid value, upgrade the bio-oil, and improve the compatibility with engines [7]. Metal oxides consist of positive metal ions and negative oxygen ions, possessing Lewis's acids and Bronsted bases. Therefore, metal oxides have acid-base or redox properties [3]. Many typical metal oxides, including CaO, MgO, and ZnO, have been utilized to enhance bio-oil properties during the pyrolysis of waste oils [8]. In general, the temperature is mainly influence to convert the long chain fatty acid into middle chain hydrocarbon molecule, and the effects of the catalyst and its surface area accelerate the dehydration and decarboxylation reaction. Then, a middle chain hydrocarbon molecule was created to produce a component of gas oil and gas oil fractions into a diesel-like fraction which occurs at the surface of a basic metal oxide catalyst.
CaO shows better performance in the reduction of acids and improvement of hydrocarbons and leads to a high bio-oil HHV, which converts those acids into hydrocarbons CO, CO_2, and CH_4 [9,10].

Pyrolysis requires enough thermal energy to break chemical bonds in waste oil. The specific high temperature and reactor design allowing heat and mass transfer are considered. There is a restriction that both low heat and mass transportation induce the production of bio-syngas and char. The various reactor configurations play roles in different heat-mass transfers and affect the energy efficiency, product properties, economic benefits, and environmental impact [10]. Generally, the studied process is batch and continuous, and the catalyst was packed into the reactor before the reaction started.

Objectives

This research aimed to produce liquid fuel using waste from vegetable oil by catalytic pyrolysis using calcined dolomite as a catalyst in a continuous pilot reactor. Therefore, this research was divided into two parts: **the 1st part** was the experiment in the bench reactor to determine the optimum conditions, especially the reaction temperature and catalyst loading, which affected the liquid fuel yield and the product distribution, and **the 2nd part** was the production of liquid fuel from the raw material mentioned in the pilot screw reactor with a feed rate of 800 kg/day to determine the optimum operating conditions that gave both of highest percentage yield and the product distribution in kerosene-liked ranges and further determined an economic analysis of the suitability of producing an aviation biofuel from waste fatty acids.

Methods

Raw material

Waste palm oil (WPO), cooking oil (UCO) and animal fat (AF) were used as raw materials for catalytic pyrolysis. WPO were received from Palm oil industrial company in Surat Thani province, Thailand while UCO and AF were collected from used oil company in Bangkok and Nakornpratom, respectively. The fatty acid composition of the three raw materials was analyzed by Agilent GC 7890/GCMS 5978 gas chromatograph-mass spectrometry (Agilent Technologies, USA).

Gas and solvent

Nitrogen gas (99.5% purity) used as the carrier gas was supplied by Enviromate Co., Ltd. Bangkok, Thailand. Commercial-grade (minimum of 80% purity) toluene was used as the solvent without further purification.

Catalyst

Dolomite is an anhydrous carbonate mineral composed of calcium magnesium carbonate, ideally $CaMg(CO_3)_2$, which was received from the dolomite mine at Kanchanaburi. Raw dolomite was calcined at 800 °C for 3 hours to become calcium and magnesium oxide or dolomite calcined (DC), which was used as a catalyst in this study. X-ray fluorescence (XRF) analysis was used to analyze the element composition. A D8-advance diffractometer (Bruker, Germany) was used to analyze the DC to determine the molecular structure of crystals with Cu-Kα radiation, operating the X-ray tube at 45 kV and 35 mA and scanning the samples at angles (2θ) from 10° to 80°.

Experimental procedure

Catalytic pyrolysis was carried out in two-scale reactors. A horizontal cylinder 10 cm in diameter and 45 cm in length was used to determine suitable parameters, such as reaction temperature and catalyst loading. For operation in a bench scale reactor, approximately 500 g of WPO and 1, 3 and 5 wt% DC catalyst were loaded into the reactor. Prior the test of each operation, the reactor was flown with nitrogen gas to remove air. The reactor was heated from room temperature to the set temperature (400, 425, and 450 °C) and held until the end of the reaction. After cooling the reactor at the end of the reaction, the oil product and solid were collected and weighed. Another operation was performed in a pilot screw pyrolyzer, composed of 6 screws in cylinders 10 cm in diameter and 4 m in length consecutively installed vertically was equipped inside a kiln. The vapor of oil vapor conducted with low negative pressure was collected in two condensers. The non-condensable gas product was recycled and added to biomass used as fuel to heat the reactor system. The flue gas from combustion inside the kiln was cleaned by a wet scrubber and then purged out. The continuous operating condition of the screw reactor was adopted from the bench reactor. Figure 1 shows both reactor types.

The liquid and solid products were collected for determination of the yield of liquid and solid char while the gaseous product was calculation by difference method on the mass balance, where the yield was calculated from Equation (1),

$$\text{Yield (wt\%)} = \frac{\text{desired product (g)}}{\text{initial of WPO (g)}} \text{ x } 100 \qquad (1)$$

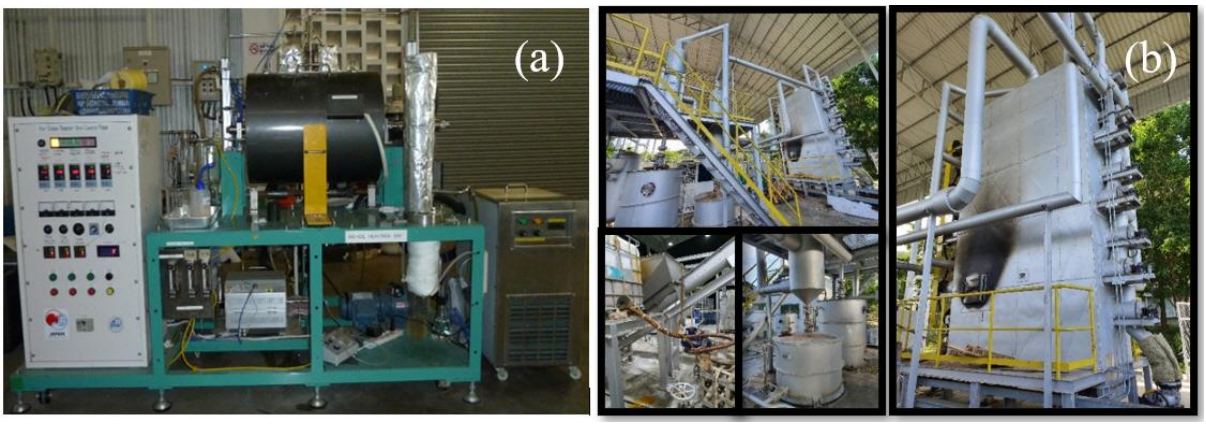

Figure 1. a) A bench scale reactor. b) A pilot screw pyrolyzer.

The gaseous products were collected with a syringe into gas bags to analyze the composition using GC on an HP5890 series II gas chromatograph that was equipped with both flame ionization and temperature-controlled detectors. Order to analysis of the liquid biofuel was conducted using GC-MS with the injector set to 250 °C and helium as the carrier gas. Identification of the components was accomplished by comparison with the NIST database. The biofuel product was analyzed by a simulated distillation gas chromatograph (SimDis) according to the ASTM D2887 standard, and the five fractions of the liquid product also consisted of gasoline (IBP–220 °C), kerosene (221–250 °C), diesel (251–350 °C), gas oil (351–370 °C) and long residues (371 °C–FBP), were identified and recorded [8,9]. The properties of biofuel were characterized in terms of the heating value using an AC-350 calorimeter (LECO Instrument, USA.), a kinematic viscosity at 40 °C in accordance with ASTM D445 using a KV-6 viscometer bath (Stanhope-Seta, UK.) and acidity using a 916 Ti-Touch automatic titrator (Metrohm AG, Germany).

Results

This research aimed to determine the suitable conditions to produce aviation biofuel via waste vegetable oil pyrolysis in two types of reactors: bench scale and pilot reactor. Therefore, this research work was divided into 2 parts as follows, and the cost of production was proposed.

Characteristics of the raw material and catalyst

Table 1 shows the types of fatty acids in the WPO, UCO and AF. The fatty acid composition in WPO was 0.93 wt% myristic acid, 44.63 wt% palmitic acid, 2.56 wt% stearic acid, 39.56 wt% oleic acid, and 9.56 wt% linoleic acid. The composition in UCO was close to that in WPO in that UCO had myristic, palmitic, stearic, and linoleic acids of 0.87, 35.69, 4.48, 45.96 and 11.84 wt%, respectively, due to cooking oil in Thailand produced from palm oil. AF had quite different fatty acids, especially palmitic and linoleic acids, which were 21.62 and 25.11 wt%, respectively.

Table 1. Composition of fatty acids in raw material.

component of fatty acid	fatty acid (wt%)		
	WPO	**UCO**	**AF**
Saturated			
myristic acid, C14:0	0.93	0.87	0.74
palmitic acid, C16:0	44.63	35.69	21.62
stearic acid, C18:0	2.56	4.58	4.73
Other	1.69	0.65	2.46
Total	49.81	41.79	29.55
unsaturated			
oleic acid, C18:1	39.56	45.96	38.48
linoleic acid, C18:2	9.56	11.84	25.11
Other	1.07	0.41	6.86
Total	50.19	58.21	70.45

The natural dolomite was calcined at 800 °C for 3 h to produce MgO and CaO. The XRF analysis composition of calcined dolomite is mainly CaO and MgO at 59.80 and 33.50 wt%, respectively. Figure 2 illustrates the XRD pattern and the peak of the natural source of dolomite. The compound of $CaMg(CO_3)_2$ is presented in the form of $CaCO_3$ and some CaO and MgO, as shown in Figure 2(a), which is the main element in natural dolomite. In the pyrolysis process, dolomite should be in the form of MgO and CaO, which can accelerate the reaction in the process. This optimum condition which retreated dolomite by the calcination at 800 °C for 3 hours, was observed [11]. The carbonate of natural dolomite after calcination was removed and converted to CaO, $Ca(OH)_2$, MgO and $Mg(OH)_2$. Figure 2(b) represented the XRD pattern of the calcined dolomite exhibited the obvious characteristic diffraction peaks of CaO at 2theta of 22.1°, 28.9°, 36.7°, and 44.6°, while MgO exhibited the characteristic diffraction peaks of metal at 42.3° and 61.8°. This result suggested that almost all $CaMg(CO_3)_2$ phases could be reduced into CaO and MgO during the calcination process. Particularly, a basic metal oxide catalyst such as MgO has been used as a catalyst enhance to promote thermal decomposition and further catalytic cracking over basic active site at the catalyst mesoporous surface structure resulting to produced a lower oxygen content and shorten hydrocarbon chain while CaO could act both of an absorbent and catalyst depending on the process conditions, The use of CaO promoted decarbonylation reactions during catalytic cracking, leading to the enhanced formation of CO. Therefore, this study was performed via the catalytic cracking reaction using both MgO and CaO that also favor decarboxylation in the pyrolysis process and enhance to improve the conversion of raw material enable to maximized a diesel-liked fraction [12].

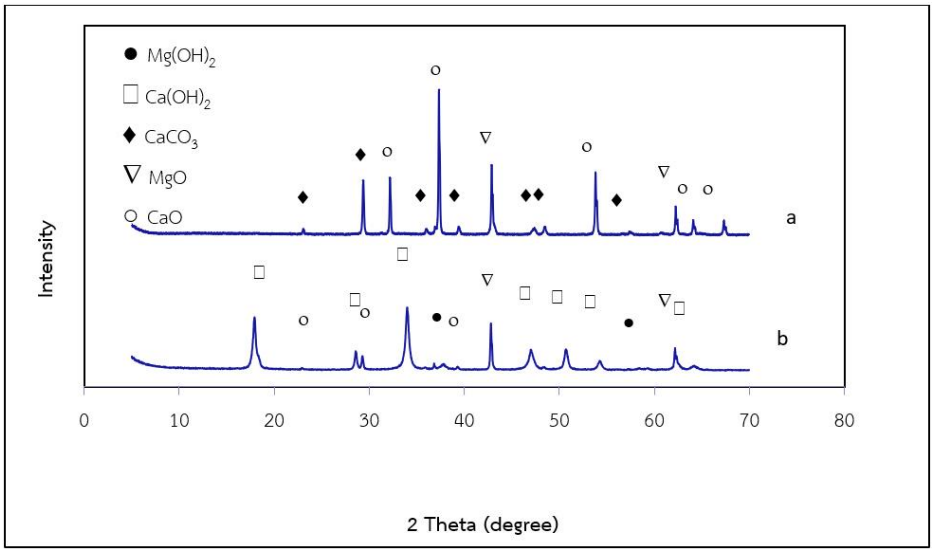

Figure 2. XRD of dolomite calcined (a) Natural dolomite (b) Dolomite calcined at 800 °C for 3 h.

The BET surface area, pore volume and average pore size before and after calcination are presented in Table 2. The BET surface area, pore volume and average pore size after calcination were 21.4045 m/g, 0.2597 cm^3/d and 22.12 A, respectively, which were larger than the values before calcination due to the composition of dolomite also was arrangement by the release of CO_2 during calcination. Figure 3 illustrates that in the comparison of SEM images, surface-calcined dolomite formed uniform particles, resulting in a higher surface area.

Table 2. Properties before and after calcination.

natural dolomite	**BET area, m^2/g**	**pore volume, cm^3/g**	**average pore size, A**
before calcination	8.00	0.02	9.73
after calcination	21.40	0.26	22.12

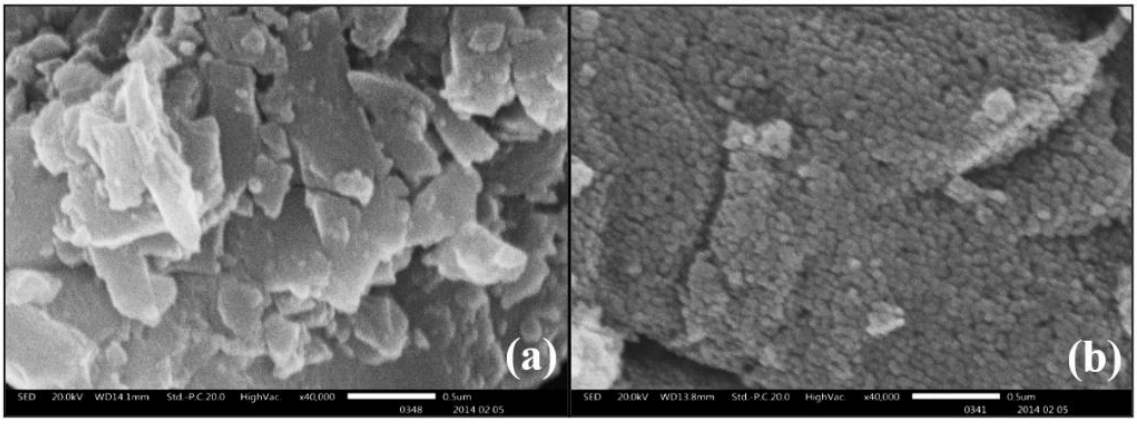

Figure 3. SEM image (a) natural dolomite (b) dolomite calcined at 800 °C for 3 hr.

The optimal conditions in a bench reactor

This part of the experiment observed the effect of parameters such as the percent loading of catalyst and reaction temperature on the product yield and composition in the liquid product using WPO as the representative raw material. Then, the optimum conditions were determined.

Effect of catalyst loading on product yield and composition in liquid product

The yield and composition of the liquid product are expressed in Tables 3 and 4, respectively. The liquid product yields without and with 1 wt% catalyst was not significantly different, whereas 3 wt% and 5 wt% gave the same yield and were higher than 1 wt% which illustrated in Table 3. The composition in the liquid product contributed the highest fraction of kerosene at 23.72% at 3 wt% catalyst. In conclusion, when using catalyst loading of 3 wt% was selected as the optimum condition to produce kerosene.

Table 3. Effect of catalyst loading on product yield.

Experiment	product yield (wt%)		
	solid	liquid	gas
non catalyst	9.56	64.25	26.19
1 wt%	7.23	65.23	27.54
3 wt%	3.43	68.22	28.35
5 wt%	2.36	68.25	29.39

Table 4. Effect of catalyst loading on liquid product composition.

experiment	product distribution (wt%)			
	naphtha	kerosene	diesel	residue
WPO	0.00	10.00	10.00	80.00
non catalyst	11.60	12.40	46.50	29.50
1 wt%	13.20	18.90	51.70	16.20
3 wt%	14.72	23.72	51.24	10.32
5 wt%	16.26	21.37	50.20	12.17

Effect of temperature on product yield and composition in liquid product

The reaction was carried out at temperatures of 400, 425 and 450 °C by using the same catalyst loading of 3 wt%. The results of the yield and composition of the liquid product are illustrated in Figures 4 and 5, respectively. Figure 4 shows the highest liquid yield at 425 °C. Figure 5 shows that the kerosene composition in the liquid product slightly increased with reaction temperature. It was observed that temperatures of 425 and 450 °C gave the same and lower residue than 400 °C, whereas both temperatures produced almost the composition of kerosene as 22 wt.%. The increase in reaction temperature favors the reaction rate, resulting in an increasing liquid yield [1,9]. However, too high of a temperature also converts lower liquid and high gas

yields. The reaction temperature of 425 °C was determined as an optimal temperature. In conclusion, the optimum parameters were 3 wt% catalyst and 425°C.

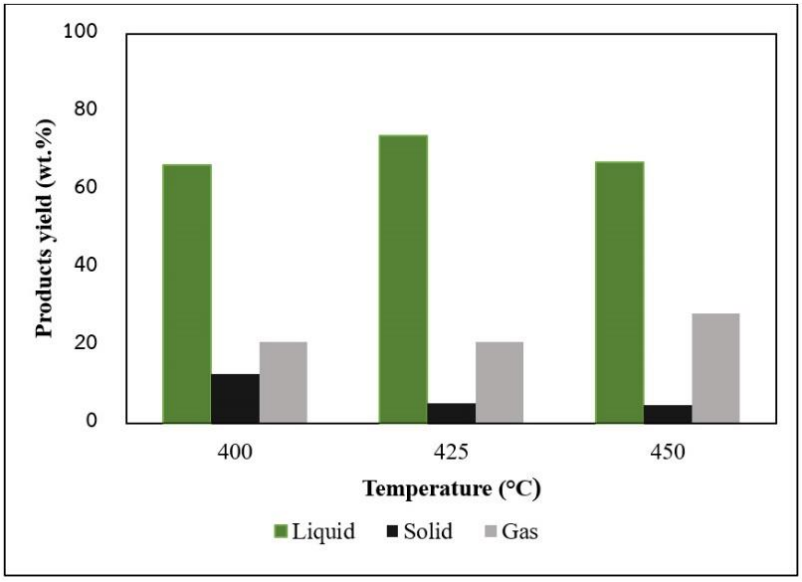

Figure 4. The effect of temperature on product yield.

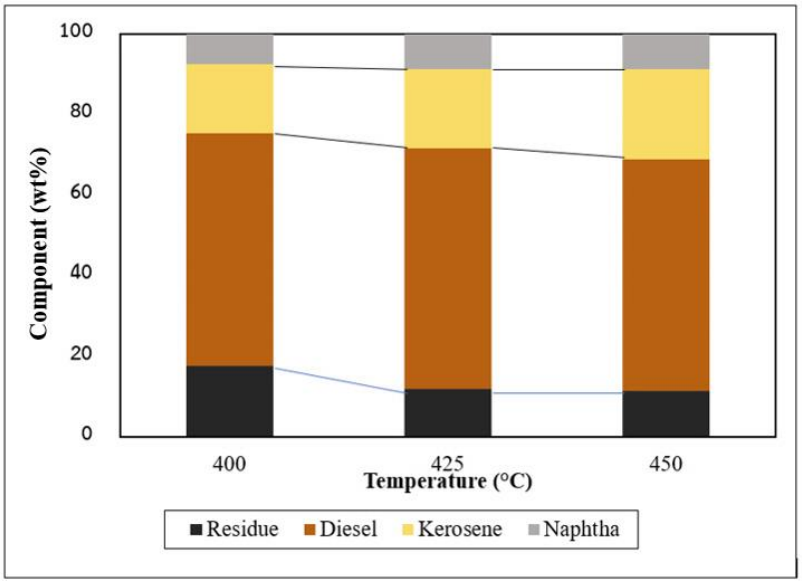

Figure 5. The effect of temperature on the composition of the liquid product.

The 2nd part was the production of liquid fuel from the raw material mentioned in the pilot screw reactor.

This part employed the optimum conditions from the 1st part, such as 3 wt% catalyst loading and 425°C reaction temperature for continuous operation with a feed rate of 800 kg/d. Three raw materials were used for this study: WPO, UCO and AF. Prior the test, a moisture content less than 10 wt% was controlled by evaporation. The higher heating value of raw materials such as WPO (26 MJ/kg), UCO (24.36 MJ/kg) and AF (24.20 MJ/kg) while the acid values of WPO, UCO and AF were 8.95, 5.76 and 4.81 mg KOH/g, respectively.

Conclusions and Discussion

The results of continuous operation of the reaction in the pilot screw reactor are expressed in Table 5 and Table 6. The product yield of each raw material can be seen in Table 5. UCO presented the highest yield of liquid product (69.25 wt%), whereas AF gave the lowest (61.52 wt%). In consideration of the composition in the liquid product of each raw material, as seen in Table 6, it was observed that the three raw materials gave almost the same composition. In particular, a kerosene fraction was in the range of 21.95 to 23.90 wt%. This is because the components of the three types of raw material have almost the same fatty acids. In addition, comparing the composition before and after the reaction of WPO, the majority of the residue fraction on raw WPO (80.55 wt%) was converted the most and remained at 5.58 %. The fuel properties of pyrolysis oil obtained from WPO, UCO and AF represented the higher heating value of 28.71, 27.98, 26.62 MJ/kg that higher than that raw material before fed into the pyrolysis reactor. The acid values of the liquid product after pyrolysis of WPO, UCO and AF were reduced to 0.83, 0.66 and 0.57 mg KOH/g, respectively. The kinematic viscosity of pyrolysis oil obtained from WPO, UCO and AF were 16.34, 14.41, 15.62 mm^2/s. The results in this study conform to several studies showing that CaO or MgO reduced the acid value of pyrolysis oils [8,9]. It was mentioned above that this is an alternative method to produce kerosene by pyrolysis, which is cheaper than hydrocracking using hydrogen, which is a severe process. The disadvantage of pyrolysis is that only 20 wt% of kerosene is present in the liquid product; however, other fractions, such as naphtha, diesel and fuel oil, are valuable after distillation. In addition, the process needed to keep a standard of aviation biofuel after kerosene separation.

Table 5. Product yield of each experiment.

raw material	product yield (wt%)		
	liquid	solid	gas
waste palm oil (WPO)	66.58	8.08	25.34
used cooking oil (UCO)	69.25	10.23	20.52
animal fat (AF)	61.52	12.10	26.38

Table 6. The effect of different raw materials on liquid yield and composition.

Raw material	product distribution (wt%)				
	yield	naphtha	kerosene	diesel	residue
raw waste palm oil	n./a.	0.00	9.75	9.70	80.55
waste Palm oil (WPO)	66.58	21.63	23.57	48.22	5.58
used cooking oil (UCO)	69.25	22.90	23.90	47.83	5.37
animal fat (AF)	61.52	24.84	21.95	46.65	6.56

Cost estimation for liquid product from pyrolysis and kerosene production

The cost of kerosene production was estimated by using the following hypotheses:

(1) WPO used a raw material feedstock

(2) The basis of calculation: 1 month operation with 800 kg/d feeding rate

(3) The conversion of WPO to liquid fuel of 66.58 wt% or production rate of 16,000 kg/month

(4) kerosene composition 20% approximately of 3,200 kg/month

(5) The estimate WPO price of 15,000 baht/ton

Table 7 represents the assumption and parameters of the cost analysis, especially the cost of raw material, which shared 74%, which was the main factor. After summation of the operating and investment costs, the total cost of kerosene was 34.75 baht/kg. However, kerosene-liked fraction was not largely produced by this process, but the total cost of production was quite low compared with the FT or hydrocracking process [10], for which the price was 133 baht/kg.

Table 7. Cost business analysis of kerosene production.

	item	quantity	per unit	amount	%
1	WPO	24 t	15,000 baht/t	360,000	74.36
2	wood chip for heating	20 t	1,500 baht/t	30,000	6.20
3	electricity			17,500	3.61
4	activated clay and filtration	12,000/l	0.80 baht/l	9,600	1.98
5	maintenance			5,000	1.00
6	labors	6 persons	10,000 baht/month/person	60,000	12.40
7	miscellaneous			2,000	0.45
	Total			484,100	100%
	operating cost per kg of pyrolysis oil (baht/kg)			30.25	
	operating cost of kerosene from pyrolysis oil (baht/kg)			30.25	
8	separation for kerosene (baht/kg of kerosene)			2.50	
	total operating cost of kerosene (baht/kg)			32.75	
9	Investment cost (baht/kg)			2.00	
	Total cost of kerosene (baht/kg)			34.75	

Waste palm oil, cooking oil, and animal fat were used as raw materials for biofuel production by using calcined dolomite as a catalyst in a pilot plant in Saraburi. The WPO pyrolysis helped to determine the optimum conditions at a catalyst loading of 3 wt% and a reaction temperature of 425 °C. This condition was employed to operate in the pilot reactor. Pyrolysis of 3 types of raw material in the pilot reactor gave a product yield range of 61-69%. The composition in liquid biofuel was composed of naphtha, kerosene, diesel and fuel oil, in which kerosene shared approximately 21.95 to 23.90 wt%. The estimated cost per kg of aviation biofuel (Kerosene) for the production of 800 kg/d, including operating and investment costs, was 34.75 baht/kg. The advantage of this process is lower cost production than the FT synthesis process and vegetable hydrocracking, whereas the disadvantage is that only 25% of aviation fuel is produced from the total liquid yield.

References

[1] Kraiem, T., Hassen, A. B., Belayouni, H., and Jeguirim, M. (2017). Production and characterization of bio-oil from the pyrolysis of waste frying oil. *Environ. Sci. Pollut. Res*., *24*(11), 9951-9961.

[2] Su, G., Ong, H. C., Ibrahim, S., Fattah, I. M. R., Mofijur, M., and Chong, C. T. (2021). Valorization of medical waste through pyrolysis for a cleaner environment: Progress and challenges. *Environ. Pollut*, *279,* Article 116934.

[3] Ong, H. C., Chen, W.-H., Farooq, A., Gan, Y. Y., Lee, K. T., and Ashokkumar, V. (2019). Catalytic thermochemical conversion of biomass for biofuel production: A comprehensive review. *Renew. Sustain. Energy Rev*., *113,* Article 109266.

[4] Ahmed, M. H. M., Batalha, N., Mahmudul, H. M. D., Perkins, G., and Konarova, M. (2020). A review on advanced catalytic copyrolysis of biomass and hydrogen-rich feedstock: Insights into synergistic effect, catalyst development and reaction mechanism. *Bioresour. Technol*, *310.* Article 123457.

[5] Escola, J. M., Aguado, J., Serrano, D. P., and Briones, L. (2014). Transportation fuel production by combination of LDPE thermal cracking and catalytic hydroreforming. *J. Waste Manag, 34*(11), 2176-2184.

[6] Trabelsi, A., Zaafouri, K., Baghdadi, W., Naoui, S., and Ouerghi, A. (2018). Second generation biofuels production from waste cooking oil via pyrolysis process. *Renew. Energy*, *126*. 888-896.

[7] Xu, J., Jiang, J., Sun, Y., and Chen, J. (2010). Production of hydrocarbon fuels from pyrolysis of soybean oils using a basic catalyst. *Bioresour. Technol*, *101*(24). 9803-9806.

[8] Bhoi, P. R., Ouedraogo, A. S., Soloiu, V., and Quirino, R. (2020). Recent advances on catalysts for Improving hydrocarbon compounds in bio-oil of biomass catalytic pyrolysis. *Renew. Sustain. Energy Rev*., *121*, Article 109676.

[9] Wang, S., Yuan, C., Esakkimuthu, S., Xu, L., Cao, B., Abomohra, E. F., Qian, L., Liu, L., and Hu, Y. (2019). Catalytic pyrolysis of waste clay oil to produce high quality biofuel. *J. Anal. Appl. Pyrolysis, 141*, Article 104633.

[10] Hussain, A., Santhoshkumar, A., and Ramanathan, A. (2020). Assessment of pyrolysis waste engine oil as an alternative fuel source for diesel engine. *J. Therm. Anal. Calorim*, *141,* 2277-2293.

[11] Yoosuk, B., Udomsap, P., and Puttasawat, B. (2011). Hydration–dehydration technique for property and activity improvement of calcined natural dolomite in heterogeneous biodiesel production: Structural transformation aspect. *Appl. Catal.*, *395*(1-2). 87-94.

[12] Charusiri, W., and Vitidsant, T. (2017). Upgrading bio-oil produced from the catalytic pyrolysis of sugarcane (*Saccharum officinarum* L) straw using calcined dolomite. *Sustain. Chem. Pharm*, *6*, 114-123.