Catalytic Pyrolysis Of Coconut Oil

by Catalytic Pyrolysis Of Coconut Oil Catalytic Pyrolysis Of Coconut Oil

ORIGINAL ARTICLE

Catalytic pyrolysis of coconut oil soap using zeolites for bio-hydrocarbon production

Teguh Kurniawan[1] · Achmad Setiawan[1] · Nurika Andana Putri[1] · Anton Irawan[1] · Asep Bayu Dani Nandiyanto[2] · Yazid Bindar[3]

Abstract

Soap pyrolysis is an interesting route for green jet fuel production because it is a simple process without required hydrogen supply and operated under atmospheric pressure. However, coke as an undesired product is often formed in high yield. In this investigation, pyrolysis of coconut oil soap was performed via catalytic routes in a batch reactor to avoid excessive coke formation. Two zeolite types, faujasite (H-Y) and mordenite (H-M), were evaluated as catalysts for pyrolysis. Catalyst loadings were studied for H-Y 20%, 40%, and 60%. Product analysis was performed by gas chromatography-mass spectrometry (GC-MS) to identify bio-oil components. Physical properties analysis was performed to determine the density and viscosity of the bio-oil product. The bio-oil produced from thermal process is composed of olefins C_6–C_{18} (43.4%), ketones (38.6%), and paraffins C_7–C_{18} (14.8%). Thermal pyrolysis showed low yield bio-hydrocarbon (olefins and paraffins) C_8–C_{16} (11%) and high solid residual formation (23.4%). Catalytic pyrolysis using zeolites of reduced solid residual formation to 10.6% with high bio-oil yield; however, the undesired carboxylic acid products were produced. Catalyst loading effect shows that the higher catalyst loadings reduced solid residual formation with the carboxylic acid products increased. The highest bio-hydrocarbon yield (13.2%) was achieved over H-Y loading 20%. Soap pyrolysis over catalyst H-M showed high bio-oil yield (28.6%) and high bio-hydrocarbon yield (17.6%) as compared to the H-Y catalyst. The main products of pyrolysis bio-oil over H-M are olefins C_6–C_{18} (48.9%), ketones (24.5%), and paraffins C_7–C_{18} (15.9%). The range of bio-hydrocarbon produced was mainly similar to jet fuel. Catalytic pyrolysis route using zeolites improved the quality of bio-oil and reduced coke formation.

Keywords Pyrolysis · Zeolite · Coconut oil soap · Bio-hydrocarbon · Green jet fuel · Coke

1 Introduction

Fossil fuel depletion is unavoidable due to its nature as a non-renewable material while it consumes continuously since the industrialization era. The emission of greenhouse gasses from the combustion of fossil fuels is the main contributor to global warming. Transportation sectors depend heavily on fossil fuel.

For example, aviation industry fuel consumption reached 1.4 million barrels per day in USA in the beginning year of 2020 [1]. Electric car is currently become trend to substitute the conventional fossil fueled car; however, the electric aircraft still needs time to be ready to be commercialized. Electric aircraft commercialization is restricted with current status of battery with specific energy of only 200 Wh/kg which means 1.7% of the jet fuel energy content [2]. Low specific energy of battery becomes the main obstacle to use electric aircraft in near futures. Hence, green fuel from renewable sources would be potential alternative to substitute fossil fuel before the electric aircraft technology commercially applicable.

Various feedstocks could be employed for bio-hydrocarbon production such as plant/animal oil, lignocellulosic biomass, sugar-rich material, and solid fraction of municipal solid waste [3]. Plant or animal oil is among potential feedstocks for green fuel production. Several process technologies routes have been developed to produce green jet fuel

✉ Teguh Kurniawan
teguh@untirta.ac.id

[1] Department of Chemical Engineering, Universitas Sultan Ageng Tirtayasa, Cilegon 42435, Indonesia

[2] Department of Chemistry, Universitas Pendidikan Indonesia, Bandung 40154, Indonesia

[3] Department of Chemical Engineering, Institut Teknologi Bandung, Bandung 40132, Indonesia

Ⓢ Springer

from plant/animal oil such as transesterification, direct pyrolysis, hydrodeoxygenation (HDO), and soap pyrolysis [4, 5]. Commercial technology using HDO requires hydrogen which is expensive and needs high-pressure operation. Simple process technology such as soap pyrolysis was established during the Second World War in China to produce gasoline and diesel oil from tung oil soap [6]. Process block diagram of soap pyrolysis is presented in Fig. 1. Saponification of vegetable oil with a basic solution followed by pyrolysis produced bio-oil which then is distilled into gasoline, jet fuel, and diesel oil. The soap pyrolysis route is rather simple process, i.e., operated under atmospheric pressure operation and no hydrogen requirement, instead of other complicated routes to produce bio-hydrocarbon fuel.

Table 1 presents a literature survey in soap pyrolysis to produce bio-hydrocarbon. Temperature operating of pyrolysis affects the yield of pyrolysate products, particularly residual solid yield i.e. salt and coke. According to Du et al., char and coke are different depending on the mechanisms and in which part the carbon is formed. Char is formed as macromolecules on the wall of pyrolysis reactor and the external surface of catalysts, while coke is formed in the micropore of catalysts [12, 13]. Pyrolysis soap at low temperature 150–300 °C produced a high amount of residue 37–78%, while at high temperature 400 °C, residue is only 5.5% [8]. Solid residues yield was also reported high in thermal pyrolysis of palm stearine soap at a temperature of 370 °C with residual solid yield in the range of 44–57% [10]. It was also reported that feedstock soap types affected the yield of products [7]. Pyrolysis of calcium salts of tung oil was produced more residual coke (48.6%) and low yield bio-oil product (41.5%) than pyrolysis of calcium salts of stearic acid with residual coke only 17.3% and high yield oil product 76%. Tung oil consists of about 80% eleostearic acid ($C_{18}H_{30}O_2$) which has three conjugated double bonds while stearic acid ($C_{18}H_{36}O_2$) is a saturated fatty acid type. The three conjugated double bonds favored cyclization process to produce aromatic which led to further reaction into coke. Feedstock selection was crucial to obtain a high yield of bio-hydrocarbon in the bio-oil products. Lappi and Allen reported that pyrolysis of castor oil soap which is rich in ricinoleic acid ($C_{18}H_{34}O_3$) with hydroxy fatty acid, resulted in high ketone and aldehyde of bio-oil pyrolysate, while pyrolysis of palm oil soap rich in palmitic acid produced high paraffin and olefin component with low oxygenates compound [14].

Catalysts for soap pyrolysis are important to increase the reaction rate and improve product selectivity. Metals of soap have an important role as catalysts as reported in the literature [9, 10]. Mg-Fe catalyst was found to be effective in suppressing alkene production which has a negative effect on stability of green diesel produced [9]. Metal oxide such as ZnO acted as an active catalyst in the isomerization to produced isoparaffin from palm stearine [10]. The cement which mainly consists of CaO and Al_2O_3 was reported as a catalyst for sodium palm oil soap pyrolysis which was reported to reduce the oxygenated compound in the pyrolysate [8].

Zeolites are microporous crystalline materials which are well-known catalysts in refinery and petrochemical industries. Zeolite Y is among the most important catalysts in oil cracking to produce alkane, alkene, and cycloalkane. Zeolites are also found in nature in massive amounts; hence, the price is cheap as compared with synthetic zeolites. Commercial application of natural zeolites for industrial catalyst was in the selectoforming process developed by Mobil Oil for removal low octane normal alkanes by selective hydrocracking on erionite containing about one-tenth percent platinum [15]. Pyrolysis of lignin was studied by Lee et al. using natural zeolites in the pyrolysis reactor and fed into the bed of H-ZSM-5 in the sequential reactor. The series reactor configuration has decreased the coke deposition in the expensive HZSM-5 and improved the product oil quality [16].

Catalytic pyrolysis soap to produce bio-hydrocarbon using zeolites is rarely reported. We investigated pyrolysis of coconut oil soap using zeolites to synthesize green jet fuel using zeolites as catalyst. Effects of catalyst zeolite loading and zeolite type to product yield and properties were further studied. The main originalities of this studies are utilization zeolites, i.e., FAU and MOR, catalysts to reduce coke yield and improve bio-oil quality.

2 Experimental section

The research was designed to study the effect of zeolite types, i.e., H-Y and H-MOR. The effect of zeolite loading was also investigated for sample H-Y with loading 0.2, 0.4, and 0.6 g.

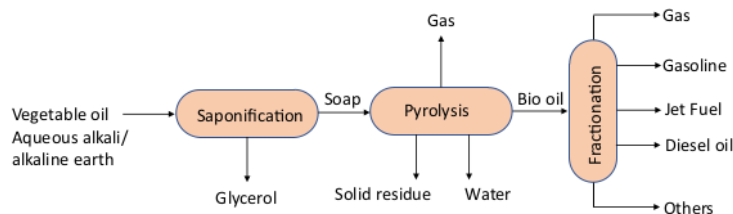**Fig. 1** Flow diagram of metal soap pyrolysis into green fuel

Table 1 Literature survey of pyrolysis oil soap investigations

Catalysts added	Metal cation	Soap types oil sources	Ratio catalyst to Soap	Reactor type/material	Pressure	Temperature	Time	% wt.				% oil yield*	Ref.
					atm	(°C)	(min)	Water	Gas	Oil	residue		
No	Ca	Tung oil	0	Batch with gas burner/cast iron	1	37–537	360	7.4	6.97	38.4	45.0	42.5	[7]
No	Ca	Stearic soap	0	Batch with gas burner/cast iron	1	37–537	360	3.13	4.31	73.5	16.70	77.8	[7]
Cement (CaO & Al$_2$O$_3$ dominant) heater/stainless steel	Na 1	Palmitic soap T room—300	30:70 75	Batch with electric 7.2	22.6	28	37.8	31.7					[8]
Cement (CaO & Al$_2$O$_3$ dominant) heater/stainless steel	Na 1	Palmitic soap T room—400	30:70 75	Batch with electric 7.0	21.0	63	5.5	70.4					[8]
No	Mg-Fe	Palm stearin	0	Batch/glass reactor	1	350	360	6.7	7.5	47.5	38.4	50.9	[9]
No	Ca-Mg-Zn	Palm stearin	0	Batch/glass reactor	1	370	300	1.6	22.8	31.1	44.4	31.6	[10]
White cement (CaO, SiO$_2$, Al$_2$O$_3$, dominant)	Not reported	tallow	1:4	Stainless steel	1	300	60	6.4	5.8	42.9	45.08	45.7	[11]

$*\%oil\ yield = \frac{\%wt.oil}{\%wt.gas + \%wt.oil + \%wt.residue}$

Catalyst preparation was conducted by ion-exchange method followed by drying and calcination. The catalysts were tested for soap pyrolysis. The detailed procedures are presented below.

2.1 Feedstock

Coconut oil soap derived from saponification of coconut oil with NaOH was purchased from a local commercial shop, CV. Bentang Terang, Indonesia.

2.2 Catalyst preparation

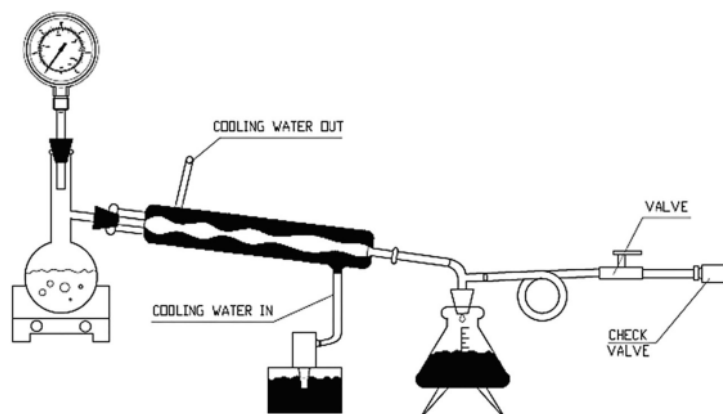Zeolite Na-Y was purchased from Advanced Chemical Supplier (ACS). According to the technical data sheet, the ratio Si to Al of zeolite Na-Y is 2.6 and Brunauer-Emmett-Teller (BET) surface area is 650 m^2/g (Table 2). Natural zeolites were obtained from Bayah, Indonesia. From our previous work, the zeolite is mordenite dominated phase with BET surface area 19 m^2/g and Si/Al = 4.4[17]. The zeolites were ion-exchanged with 2 M NH$_4$NO$_3$ solution (Sigma-Aldrich) to obtain protonated form of zeolites. The ion-exchange procedure was performed by reflux condenser for 2 h at 85 °C. The weight ratio of zeolites to ammonium was 1 to 4. The procedure was conducted two times to ensure ammonium replacing the alkali and alkaline earth metals. The ion-exchanged zeolites were dried overnight in an oven at 110 °C. The dried zeolites were calcined in a furnace at 550 °C for 8 h to obtain protonated zeolites. The samples were labeled H-Y and H-M for protonated zeolite Y and protonated natural mordenite, respectively.

2.3 Catalyst evaluation

The protonated zeolites were tested by using a pyrolysis reactor under atmospheric pressure. The experimental setup presented in Fig. 2 consists of a heater, a reactor, and a condenser. The weight ratio of H-Y to soap varied 0, 0.2, 0.4, and 0.6.

Table 2 Characteristic of zeolite sample

Zeolite sample	BET (m^2/g)	Si/Al	Framework
Bayah natural zeolites	19	4.4	MOR
Zeolite Y synthetic	650	2.6	FAU

Fig. 2 Schematic reactor for soap pyrolysis

Zeolite mordenite (H-M) was also tested at a ratio H-M to soap 0.4.

The soap and catalyst with a certain ratio were loaded into the pyrolysis reactor. The heater was turned on and temperature operation in the pyrolysis reactor is maintained to follow curve started from ambient temperature to 312 °C as presented in Fig. 3. Pyrolysis was performed under autonomous pressure. After 20 min, the heater was turned off while the condenser maintained on until the pyrolysis reactor temperature dropped to ambient temperature. Products of coconut oil soap pyrolysis were water, bio-oil, gas, and solid residue (salt, catalyst, char, and coke). All of the products were weighed, except the gas which was determined by mass balance calculation. In this study, char and coke were lumped as coke.

2.4 Product analysis

We analyzed bio-oil products of both physical and chemical properties. Physical analysis was performed using pycnometer, viscometer Cannon-Fenske for density and viscosity analysis, respectively. Specific gravity and API gravity were determined based on density and viscosity data. A gas chromatography-mass spectrometry instrument (GC-MS, GC-MS QP2010 Ultra, Shimadzu Corp., Japan) was used to
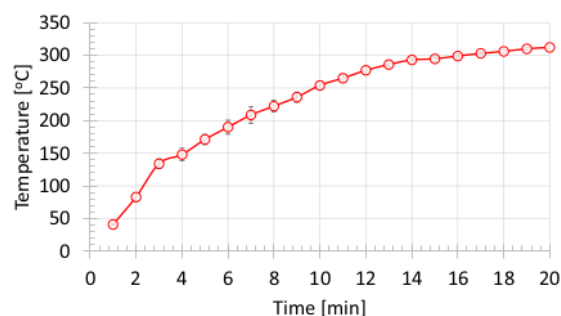

Fig. 3 Pyrolysis temperature curve

determine product component and composition. Product yield was calculated based on weight of each product (bio-oil, coke) divided by the total initial mass of soap.

3 Results and discussion

3.1 Effect of catalyst zeolite H-Y loading on product yield

Figure 4a presents the effect of catalyst zeolite H-Y loading on product yield. Soap pyrolysis without catalyst zeolite shows the highest solid residual yield 23.4%. On the other hand, pyrolysis with H-Y loading 60% shows the lowest solid residual yield of 12.4%. Solid residual most likely consisted of Na_2CO_3, coke, and unconverted soap. Catalytic pyrolysis over H-Y zeolite reduced the coke formation. There were several indications that coke reduced over H-Y, i.e., (a) the decreasing of solid residual mass and change of solid color from black in the thermal pyrolysis to brighten over H-Y 0.6 and (b) the bio-oil and water yield from pyrolysis using zeolite also increase significantly which suggested that shifting product selectivity from coke to bio-oil.

Calcium soap reported pyrolysis temperature at higher temperature 370 °C while Mg-Fe soap was pyrolyzed at 350 °C [9]. Pyrolysis temperature in this work was lower (room temperature—312 °C) than reported in the literature which was 350–400 °C. Probably, sodium soap is more active as catalyst for decarbonylation and decarbocylation; hence, the bio-oil product was formed although the pyrolysis operated at low temperature. The metal carbonate was produced through decarboxylation and decarbonylation [18, 19]. The mechanism of Na_2CO_3 formation from coconut oil soap which is mainly sodium lauric acid possibly follows Eq. 1 below. The equation was modified from literature reported elsewhere [19].

Fig. 4 Effect of catalyst zeolite
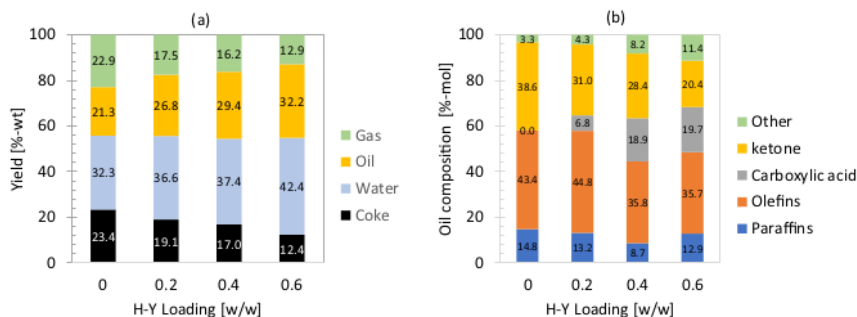H-Y loading on **a** product yield
and **b** oil composition

Table 3 Comparison of oil source and bio-oil chemical products from soap pyrolysis route

Soap types oil sources	Metals/catalyst	Paraffins (%)	Olefins (%)	Oxygenates (%)	Instrument analysis	Ref.
Coconut oil (*Cocos nucifera*)	Na/H-MOR	16	49	35	GC-MS	This work
Macauba oil (*Acrocomia sclerocarpa*)	Ca	37	42	21	GC-MS	[20]
Palm stearin (*Elaeis guineensis*)	Ca-Mg-Zn	65	35	Detected qualitatively with ferrox paper test, quantitative analysis was not performed	GC-FID for paraffin and olefin, ferrox paper test for qualitative analysis	[10]
Palm stearin (*Elaeis guineensis*)	Mg-Fe	94	6	Not reported	GC-FID with standard alkane for calibration	[9]
Palm oil (*Elaeis guineensis*)	Na	14	40	6	GC-MS	[14]
Castor oil (*Ricinus communis*)	Na	6	8	45	GC-MS	[14]
Palm oil (*Elaeis guineensis*)	Na/CaO-Al$_2$O$_3$	41	13	17	GC-MS	[8]

$$Na(OOC){-}C_{11}H_{23}{\rightarrow}C_{11}H_{22}$$

$$+ HCOONa \longrightarrow \frac{2HCOONa{\rightarrow}(COO)_2Na_2 + H_2}{(COO)_2Na_2{\rightarrow}Na_2CO_3 + CO} \quad (1)$$
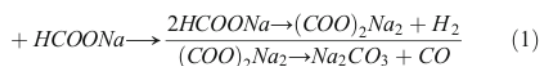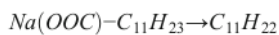
Figure 4b presents the composition of bio-oil product. It is seen clearly that olefins are the main component of bio-oil for all experiments. The metal of sodium in the soap feedstock most likely controlled the selectivity to olefins as seen in Eq. 1. Olefins as a major product were also reported by another group that used sodium metal soap as feedstock [14, 19]. Paraffin was reported as the main hydrocarbon product instead of olefins when used metal alkaline earth soaps such as calcium and magnesium soap as the feedstock [9, 10]. The impurities of products (written as other in Fig. 4b) such as 1-
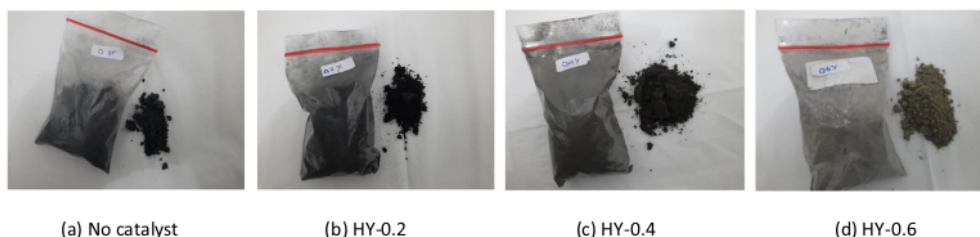

(a) No catalyst   (b) HY-0.2   (c) HY-0.4   (d) HY-0.6

Fig. 5. Spent catalyst of H-Y zeolite mixed with solid residues after soap pyrolysis. **a** No catalyst, **b** HY-0.2, **c** HY-0.4, **d** HY-0.6

Table 4 Fatty acid content of coconut oil

Fatty acid	%
C8:0	7.7
C10:0	6.1
C12:0	46.9
C14:0	17.9
C16:0	8.9
C18:0	2.9
C18:1	6.5
Other	13.1

undecanol, oleyl alcohol, and azulene in the bio-oil for pyrolysis without zeolites were identified. For pyrolysis using zeolite samples, the impurities observed were pentanol, 2-buten-1-ol, 1-heptanol, benzene, tetradecanal, and cyclododecanol. The comparison of plant oil sources and oil chemical products from soap pyrolysis route is presented in Table 3.

Figure 5 presents a picture of spent catalyst of H-Y zeolite mixed with solid residues after pyrolysis. The zeolite was effectively reduced the coke formation as seen through the colors of solid residue. A higher loading of H-Y the darkness levels of solid residue reduced significantly. Coke was formed through condensation mechanism as reported elsewhere [7]. Aromatic hydrocarbons cracked producing higher boiling aromatic hydrocarbons and further converted into asphaltenes and finally coke. According to the condensation mechanism,

the more aromatic produced, the higher the tendency of coke formation. Calcium soap of tung oil was reported to produce more aromatic instead of calcium soap of stearic acid, and as a result, the coke formation of tung oil soap pyrolysis was higher than the stearic acid soap. Zeolite with its acid sites most likely inhibited coke formation through cracking mechanism of the long hydrocarbon chain. H-Y was reported as active catalyst for cracking vacuum gas oil (VGO) with high conversion into gasoline diesel oil, kerosene, lighter component, and coke [21]. The high conversion of VGO over H-Y was attributed to its high acid site density.

Perigolo et al. investigated coke formed from pyrolysis oleic acid soap oxidized at a relatively low temperature range 300–500 °C which suggested that the coke contained reactive defective carbon [18]. Char was formed largely in the low temperature range 150–300 °C and decrease as temperature of pyrolysis increased as reported by Hussain et al. [8]. Char/coke derived from biomass pyrolysis was polyaromatics with carbonyl and hydroxyl end groups as indicated by the FTIR and Raman analyses through aldol and Diels-Alder mechanism [12].

3.2 Effect of catalyst zeolite H-Y loading on bio-hydrocarbon selectivity

Coconut oil main fatty acid composition is 47% of lauric acid ($C_{12}H_{24}O_2$) as presented in Table 4 [22]. The main component of bio-hydrocarbon product was 1-undecene ($C_{11}H_{22}$) which
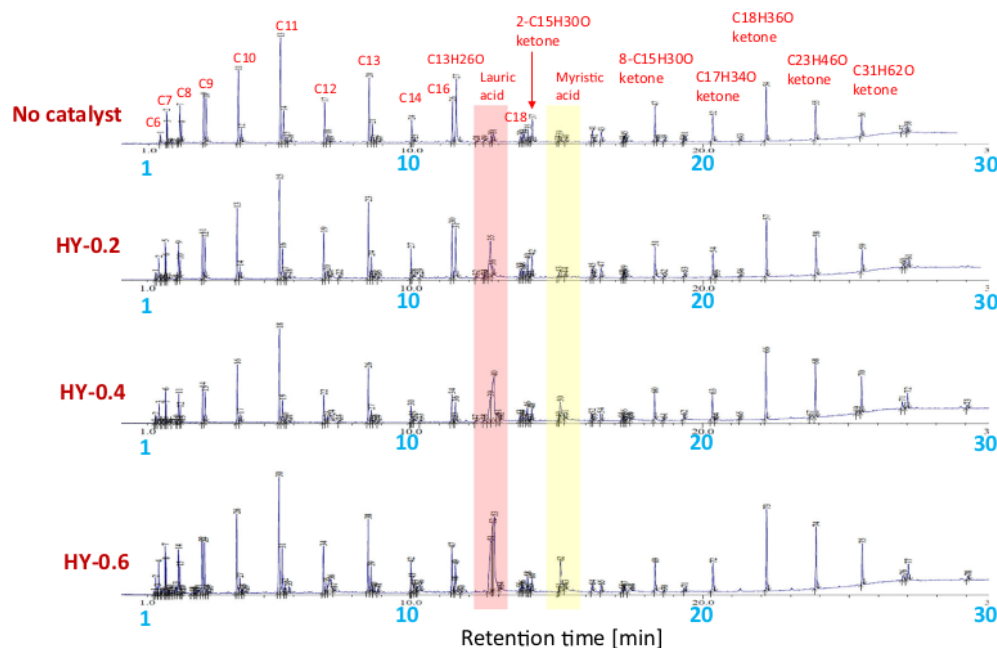
Fig. 6. Effect of catalyst loading on product composition
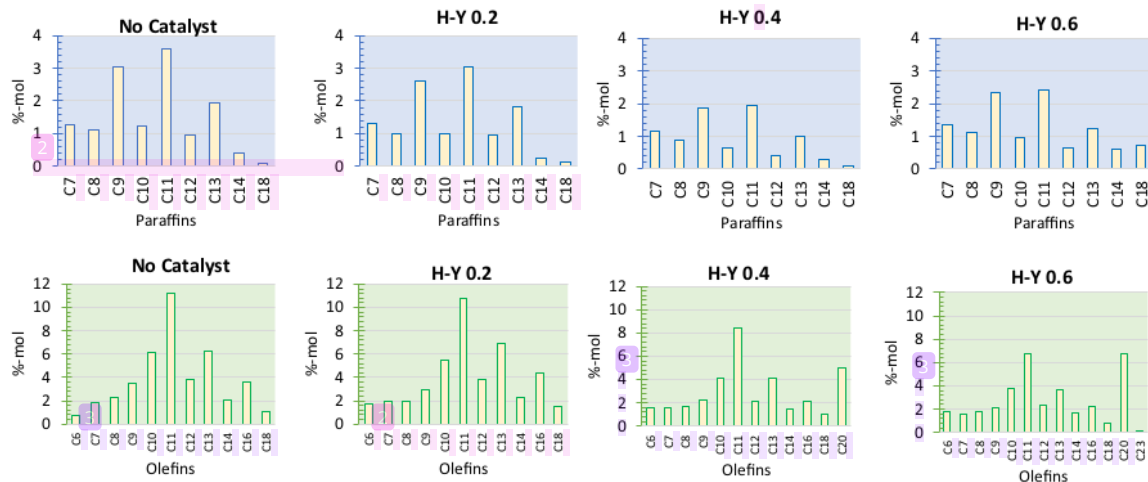
Fig. 7. Effect of catalyst zeolite H-Y loading on paraffins and olefins composition

was most likely formed from the main sodium salt fatty acid component of coconut oil (lauric acid) through the homolysis of the weakest C–C bond next to the carboxylic group [14, 23]. The bio-oil yield increase and the coke formation reduced over zeolite H-Y; however, the chromatogram area under the peaks of bio-hydrocarbon slightly decreases as seen in Figs. 6 and 7. Despite the bio-hydrocarbon percentage in the bio-oil, over zeolite H-Y was lower than without zeolite the bio-hydrocarbon yield was still high. Here, the bio-hydrocarbon yield is oil yield multiply by selectivity.

The carboxylic acid products, mainly lauric acid and myristic acid, increased in bio-oil when using zeolite H-Y during pyrolysis (Fig. 6 highlighted in red and yellow). The carboxylic acids products were not significantly detected in thermal pyrolysis without zeolite H-Y. The higher H-Y loading, the more carboxylic acids produced. Carboxylic acids formed were 6.8% at H-Y loading 0.2 and increased to 19.7% at H-Y loading 0.6. The lauric acid product is most likely formed because of hydrogen transfer between the
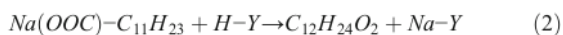
Fig. 8. Effect of H-Y loading on green fuel production
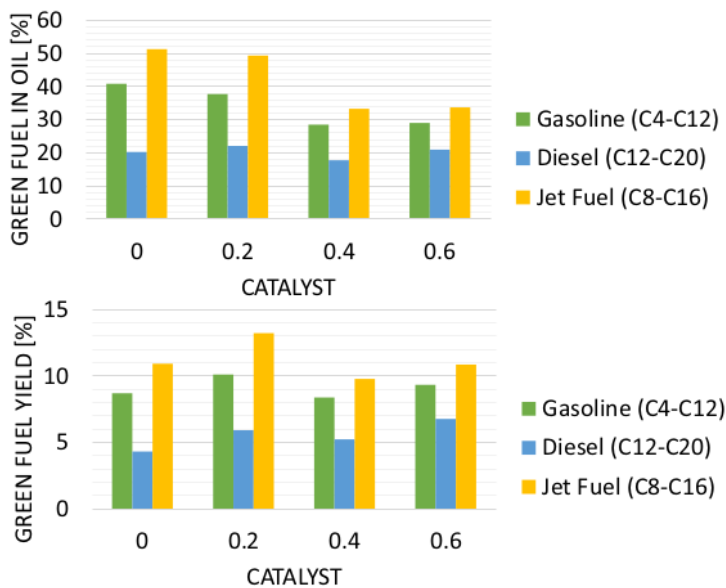
$$Green\ fuel\ yield = \%oil\ yield * \%composition$$

Fig. 9 a, b Effect of zeolite type on product yield and oil composition
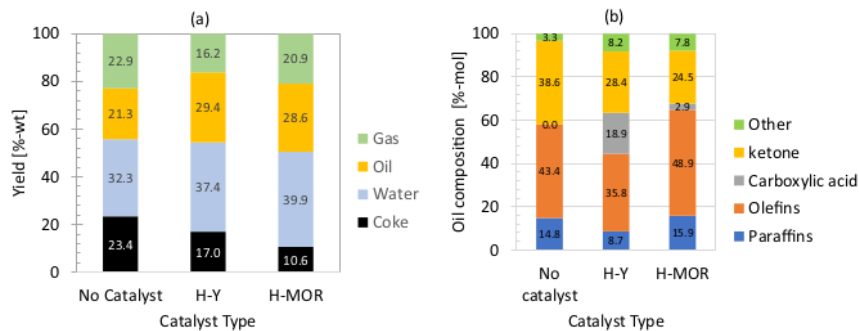
sodium soap and the protonated zeolite H-Y (Eq. 2). The more H^+ provided by zeolites, the more carboxylic acids are formed.

$$Na(OOC)-C_{11}H_{23} + H-Y \rightarrow C_{12}H_{24}O_2 + Na-Y \quad (2)$$

Bio-hydrocarbon produced via soap pyrolysis route is similar with fossil-based hydrocarbon components such as gasoline(C_4–C_{12}), diesel oil (C_{12}–C_{20}), and jet fuel (C_8–C_{16}) as seen in Fig. 8. Jet fuel range was the dominant fuel produced from the pyrolysis of coconut soap. Lauric (C12:0) and myristic acid (C14:0) as dominant fatty acids in coconut oil with 47% and 18%, respectively, determined product of bio-hydrocarbon that resulted from its homologous carbon range. HY-loading 0.2 shows the highest bio-oil yield among others.

3.3 Effect of zeolite type on product yield

Yield of solid residue over H-M is significantly low (ca. 10.6%) as compared with H-Y (ca. 17%) as seen in Fig. 9a. Surface area of zeolite-Y, 650 m^2/g, was higher than the natural zeolites with 19 m^2/g. The theoretical pore diameter of zeolite Y is 7.4 Å with a three-dimensional pore structure, while mordenite is 6.7 Å and one-dimensional pore structure only. From a textural properties perspective, zeolite Y has superiority instead of mordenite. One may expect that the coke residue over H-Y lower than mordenite. However, the results showed that solid residue of coconut oil soap pyrolysis over H-Y was higher than H-M. It is most likely the acid sites of zeolite control the coke yield. From our previous work [24], TPD ammonia results of MOR showed two buds, one in lower temperature range and the other in
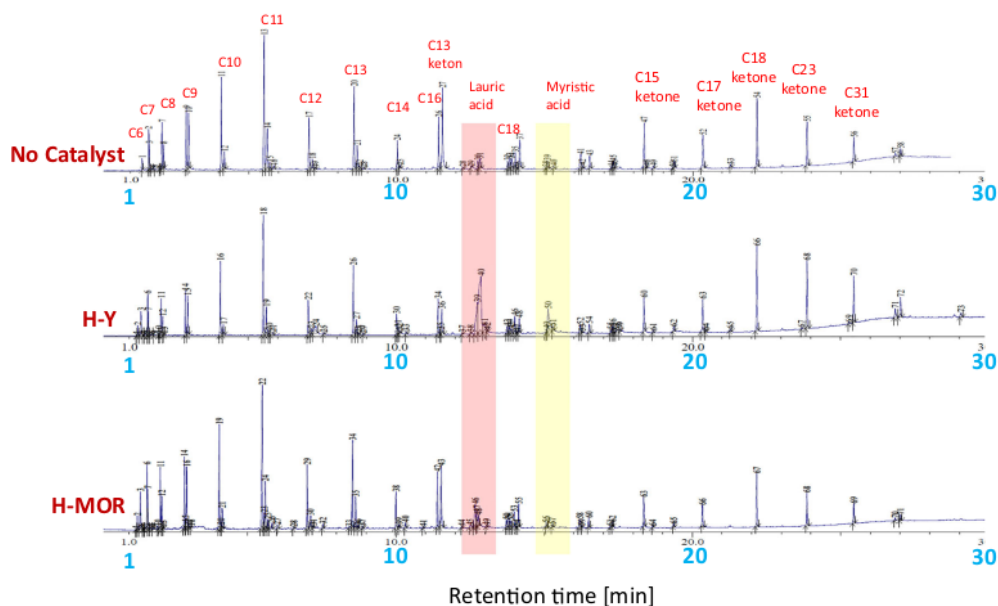

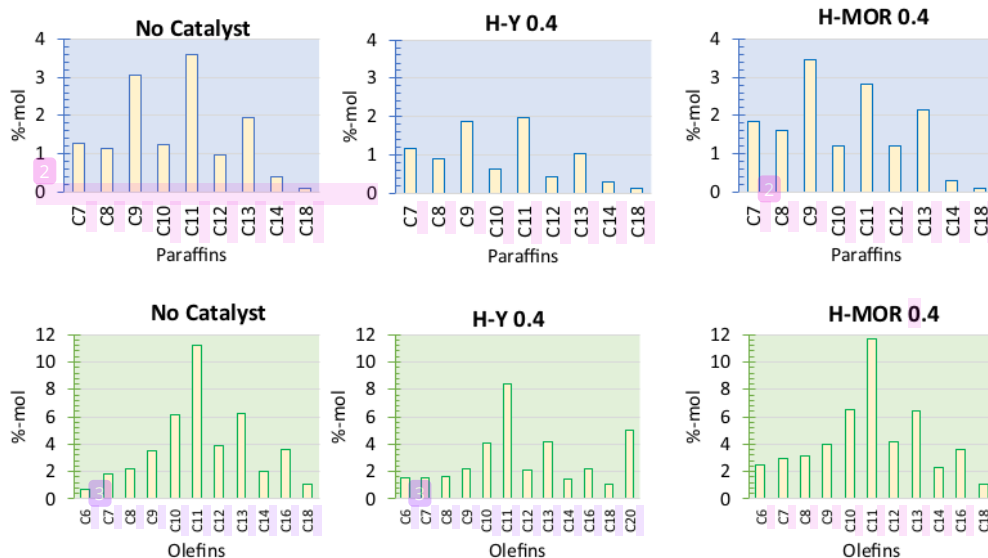**Fig. 10.** Effect of zeolite type on product composition

Fig. 11. Effect of zeolite type on paraffins and olefins composition

higher temperature range which indicated low and strong acid sites, respectively. Comparison of acidity H-Y with Si/Al 5 and H-MOR 10 with Si/Al suggested that H-M showed a number of strong acid sites higher than H-Y [25]. In the present work, zeolite H-MOR Si/Al was 4.4 and H-Y was 2.6. The high ratio of Si/Al suggested that the number of acid sites of H-MOR was lower than H-Y. Despite the number of acid sites of H-

MOR was lower than H-Y, strong acid sites of H-M were probably much higher than H-Y, hence reducing coke production.

Carboxylic acid formation was pronounced over H-Y zeolite with 18.9% instead of H-M zeolite with only 2.9% (Figs. 9b and 10). It is most likely because the ratio of Si/Al of H-Y is lower than H-M which means H-Y has high acid density. The result the H^+ available in H-Y is much higher than H-M

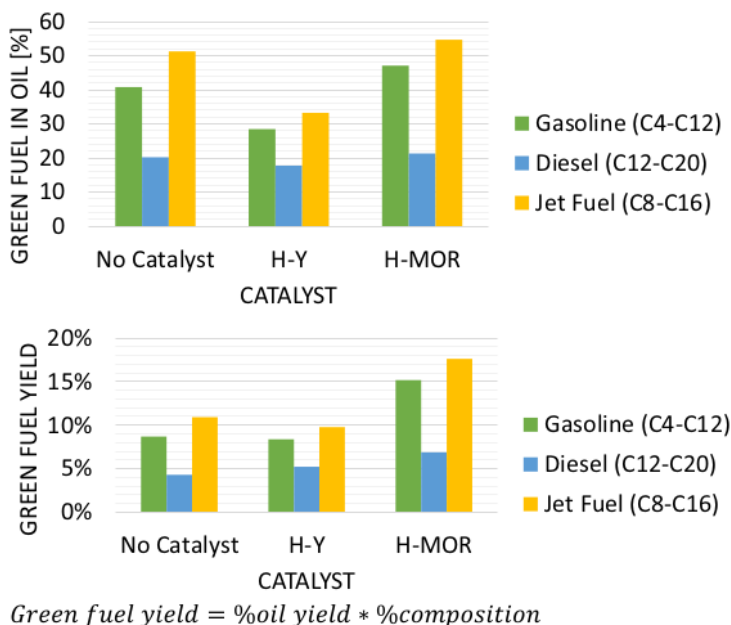**Fig. 12** Effect of zeolite type on green fuel production

$$Green\ fuel\ yield = \%oil\ yield * \%composition$$

Table 5 The effect of zeolite H-Y loading on physical properties of bio-il

H-Y loading (%-wt)	Density (g/mL)	Kinematic viscosity (cSt)	Specific gravity	API gravity
0	0.71	1.87	0.71	66.52
0.2	0.71	2.05	0.71	66.90
0.4	0.73	2.92	0.73	61.03
0.6	0.78	3.03	0.78	50.72

for H^+ transfer reaction in Eq. 2 producing more carboxylic acids. Ketone formation in bio-oil from pyrolysis over H-M was the lowest as compared with H-Y and without zeolites (Fig. 9b). According to Hsu et al., ketone was produced from splitting off carbon monoxide from the metals fatty acids [7]. Paraffin and olefins product from soap pyrolysis over H-M shows higher percentage than H-Y and without zeolite.

3.4 Effect of zeolite type on bio-hydrocarbon selectivity

Figure 11 presents the effect of zeolite type on paraffins and olefins composition. Paraffinic products detected for all samples were from C_7 to C_{18} with main components C_{11} and C_9. The percent composition of C_9H_{20} was the highest over H-M zeolite, while $C_{11}H_{24}$ was the highest on the thermal pyrolysis without zeolite. It is possible that the cracking of long-chain carbon occurred over H-M because of its strong acid sites. Olefinic products were detected within the range of C_6 to C_{18} with the main product C_{11}. The percent composition of $C_{11}H_{22}$ was the highest over H-M with almost 12% and the lowest over H-Y with 8%. The high acid density shifted partially product distributions of paraffin and olefins to carboxylic acids.

Figure 12 presents the effect of zeolite type on green fuel production. Pyrolysis of soap over H-M shows its superiority both in oil yield and bio-hydrocarbon composition, and as a result, the green fuel yield was the highest among others. Jet fuel produced over H-M was the highest with almost 18%. Natural mordenite with strong acid sites and low acid site density was suitable to reduce coke formation and to improve the green fuel yield. The low-cost of natural mordenite and extensive availability give the advantage to utilize natural mordenite as catalyst in soap pyrolysis for green fuel

production. The jet fuel could be potentially produced not only from coconut oil but also from family of coconut such as palm kernel oil of palm tree with high lauric acid content, while diesel oil is potentially produced from pyrolysis of palm stearin/palm oil soap as reported in literature [9, 10].

3.5 Effect of zeolite loading and type on physical properties

The bio-oil product of soap pyrolysis over H-Y 0.2 showed the smallest density, while the highest density number was obtained in oil produced over H-Y 0.6. The density of bio-oil increased along with the H-Y loading as seen in Table 5. This is because of the increase of carboxylic acid formation, mainly lauric acid with density 0.88 g/mL, along with the H-Y loading, while the bio-hydrocarbon composition mainly, 1-undecene with lower density 0.75 g/mL was decreased. The density of bio-oil produced from pyrolysis over H-M 0.4 and H-Y 0.4 showed similar values (Table 6). The smallest viscosity of bio-oil was obtained on pyrolysis without zeolites and the largest bio-oil viscosity was obtained when using zeolite H-Y 0.6. The higher the ratio of H-Y to soap, the higher viscosity of the resulting oil. The viscosity of bio-oil produced over H-Y 0.4 was higher H-M 0.4. It is most likely because the bio-oil from pyrolysis over H-M contains more bio-hydrocarbon C_6–C_{18} (paraffins and olefins) and low oxygenated compound C_{12}–C_{31} (carboxylic acids and ketone) which have high viscosity number.

Table 7 presents the properties of commercial jet fuel Jet A-1 [26]. It can be seen that the physical properties (i.e., density and viscosity) of the bio-oil synthesized in this work did not meet the standard specification. The bio-oil contained oxygenate and heavy carbon fractions which required separation and purification. The bio-oil needs further processing such as

Table 6 The effect of zeolite type on physical properties of bio-oil

Zeolite type	Density (g/mL)	Kinematic viscosity (cSt)	Specific gravity	API gravity
No catalyst	0.71	1.87	0.71	66.52
H-Y	0.73	2.92	0.73	61.03
H-M	0.73	2.10	0.73	61.17

Table 7 Physical properties of jet fuel (Jet A-1)

Typical properties	
Composition	
Total acidity, mg KOH/g	0.003
Aromatics, % vol	19.5
Total sulfur, % mass	0.02
Mercaptan sulfur, %mass	0.0003
Volatility	
Distillation	
Initial boiling point, °C	156
Fuel recovered	
10% vol at °C	167
20% vol at °C	172
50% vol at °C	188
90% vol at °C	234
End point, °C	258
Residue, % vol	1.0
Loss, %vol	Nil
Density at 15 °C, g/mL	0.804
Flash point, °C	42
Fluidity	
Freezing point, °C	−50
Viscosity at −20 °C, cSt	3.5

fractionation distillation to meet the commercial Jet A-1 requirement as presented in Fig. 1.

4 Conclusions

Bio-hydrocarbon was successfully produced through catalytic pyrolysis of sodium coconut oil soap over zeolite H-Y and H-M at low temperature. Zeolites successfully reduced coke formation and increased bio-oil yield which consisted of bio-hydrocarbon and oxygenate compounds. Bio-hydrocarbon produced consisted of olefins and paraffins with carbon chain length C_6–C_{18} which are potential to substitute conventional jet fuel. The solid residual yield decreased along with the increase of zeolite loading; however, the bio-oil component of carboxylic acid was increased. The combination uses of other metals soap instead of sodium and zeolites with various cations or impregnated metals, type, crystal size, and acidity could be interested to investigate in order to reduce oxygenate compounds and shifted olefinic products to more paraffins.

References

1. Barnett J Demand for jet fuel in the U.S. is recovering faster than in many other markets
2. Schäfer AW, Barrett SRH, Doyme K, Dray LM, Gnadt AR, Self R, O'Sullivan A, Synodinos AP, Torija AJ (2019) Technological, economic and environmental prospects of all-electric aircraft. Nat Energy 4:160–166
3. Morgan TJ, Youkhana A, Turn SQ, Ogoshi R, Garcia-Pérez M (2019) Review of biomass resources and conversion technologies for alternative jet fuel production in Hawai'i and tropical regions. Energy Fuel 33:2699–2762
4. Chunfei Z, Zongwei Z, Hao C, Xiangwen Z, Qingfa W (2021) Tuning hierarchical ZSM-5 for green jet fuel production from soybean oil via control of Pt location and grafted TPABr content. Catal Commun 155:106288
5. Chintakanan P, Vitidsant T, Reubroycharoen P, Kuchonthara P, Kida T, Hinchiranan N (2021) Bio-jet fuel range in biofuels derived from hydroconversion of palm olein over Ni/zeolite catalysts and freezing point of biofuels/Jet A-1 blends. Fuel 293.
6. Chang C-C, Wan S-W (1947) China's motor fuels from tung oil. Ind Eng Chem 39:1543–1548
7. Hsu H-L, Osburn JO, Grove CS (1950) Pyrolysis of the calcium salts of fatty acids. Ind Eng Chem 42:2141–2145
8. Hussain Z, Sulaiman SA, Gul H, Farooq S, Khan KM, Gulab H, Naz MY (2016) Conversion of waste-soap and soap-like materials into diesel and gasoline by catalytic pyrolysis using virgin soap as model. Can J Chem Eng 94:94–100
9. Neonufa GF, Soerawidjaja TH, Indarto A, Prakoso T (2019) An innovative technique to suppress alkene-bond in green diesel by Mg–Fe basic soap thermal decarboxylation. Int J Ambient Energy 40:374–380
10. Pratiwi M, Muraza O, Neonufa GF, Purwadi R, Prakoso T, Soerawidjaja TH (2019) Production of sustainable diesel via decarboxylation of palm stearin basic soaps. Energy Fuel 33:11648–11654
11. Hussain Z, Khan S, Rafiq M, Naz MY, AbdEl-Salam NM, Ibrahim KA (2020) Catalytic valorization of waste soap into hydrocarbon rich oil and fuel gas. Biomass Convers Biorefinery 10:1091–1098. https://doi.org/10.1007/s13399-019-00546-7
12. Du S, Valla JA, Bollas GM (2013) Characteristics and origin of char and coke from fast and slow, catalytic and thermal pyrolysis of biomass and relevant model compounds. Green Chem 15:3214–3229
13. Hilten R, Speir R, Kastner J, Das KC (2011) Production of aromatic green gasoline additives via catalytic pyrolysis of acidulated peanut oil soap stock. Bioresour Technol 102:8288–8294
14. Lappi H, Alén R (2011) Pyrolysis of vegetable oil soaps—palm, olive, rapeseed and castor oils. J Anal Appl Pyrolysis 91:154–158
15. Chen NY, Lucki SJ, Mower EB (1969) Cage effect on product distribution from cracking over crystalline aluminosilicate zeolites. J Catal 13:329–332
16. Lee HW, Kim Y-M, Jae J, Sung BH, Jung S-C, Kim SC, Jeon J-K, Park Y-K (2016) Catalytic pyrolysis of lignin using a two-stage fixed bed reactor comprised of in-situ natural zeolite and ex-situ HZSM-5. J Anal Appl Pyrolysis 122:282–288
17. Kurniawan T, Nuryoto R (2020) Characterization and application of Bayah natural zeolites for ammonium capture: isotherm and kinetic. Mater Sci Forum 988:51–64
18. Perígolo DM, de Paula FGF, Rosmaninho MG, de Souza PP, Lago RM, Araujo MH (2017) Conversion of fatty acids into hydrocarbon fuels based on a sodium carboxylate intermediate. Catal Today 279:260–266

19. Melchor JJ, Fortes ICP (2018) Bio-oil production by pyrolysis of metal soaps derived from Macauba pulp oil. J Anal Appl Pyrolysis 135:101–110

20. Fortes ICP, Baugh PJ (1994) Study of calcium soap pyrolysates derived from Macauba fruit (Acrocomia sclerocarpa M.). Derivatization and analysis by GC/MS and CI-MS. J Anal Appl Pyrolysis 29:153–167

21. Lee K-H, Ha B-H, Lee Y-W (1998) Catalytic cracking of vacuum gas oil over the modified mordenites and Y-type zeolites mixed with alumina. Ind Eng Chem Res 37:1761–1768

22. Eller Z, Varga Z, Hancsók J (2019) Renewable jet fuel from kerosene/coconut oil mixtures with catalytic hydrogenation. Energy Fuel 33:6444–6453

23. Hartgers WA, Sinninghe Damsté JS, de Leeuw JW (1995) Curie-point pyrolysis of sodium salts of functionalized fatty acids. J Anal Appl Pyrolysis 34:191–217

24. Kurniawan T, Muraza O, Hakeem AS, Bakare IA, Nishitoba T, Yokoi T, Yamani ZH, Al Amer AM (2017) Selective isomerization of n-butane over mordenite nanoparticles fabricated by a sequential ball milling-recrystallization-dealumination route. Energy Fuel 31:12691–12700

25. Jeong S, Jeon K-J, Park Y-K, Kim B-J, Chung K-H, Jung S-C (2020) Catalytic properties of microporous zeolite catalysts in synthesis of isosorbide from sorbitol by dehydration. Catal. 10:148

26. Air BP (2000) Handbook of products. Air BP, Hertfordshire, United Kingdom

Catalytic Pyrolysis Of Coconut Oil

Industrial & Engineering Chemistry Research,
2018
Publication

7   Submitted to Alfaisal University
     Student Paper   1 %

Exclude quotes   Off   Exclude matches   < 1%
Exclude bibliography   On

Catalytic Pyrolysis Of Coconut Oil

FINAL GRADE

/0

GENERAL COMMENTS

Instructor