



Teguh Kurniawan <teguh@untirta.ac.id>

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Action	Manuscript Number	Title	Initial Date Submitted	Status Date	Current Status	Date Final Disposition Set	Final Disposition
View Submission Author Response View Decision Letter View Attachments	BCAB-D-21-00404	Catalytic Pyrolysis of Coconut Oil Soap using Zeolites for Bio-hydrocarbon Production	22 Mar 2021	14 Jun 2021	Completed Accept	14 Jun 2021	Accept

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Attachments for Manuscript Number BCAB-D-21-00404 R1
"Catalytic Pyrolysis of Coconut Oil Soap using Zeolites for Bio-hydrocarbon Production"

Action	Uploaded By	Description	File Name	File Size
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Download	Reviewer 1		Review- BCAB-D-21-00404.docx	11.9 KB
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Biomass Conversion and Biorefinery

Catalytic Pyrolysis of Coconut Oil Soap using Zeolites for Bio-hydrocarbon Production

--Manuscript Draft--

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Corresponding Author:	Teguh Kurniawan, Ph.D Universitas Sultan Ageng Tirtayasa Cilegon, Banten INDONESIA	
Order of Authors:	Teguh Kurniawan, Ph.D Achmad Setiawan Nurika Andana Putri Anton Irawan, Dr-Ing. Asep Bayu Dani Nandiyanto, Dr.Eng. Yazid Bindar, Ph.D	
Corresponding Author Secondary Information:		
Corresponding Author's Institution:	Universitas Sultan Ageng Tirtayasa	
Corresponding Author's Secondary Institution:		
First Author:	Teguh Kurniawan, Ph.D	
First Author Secondary Information:		
Order of Authors Secondary Information:		
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Abstract:	<p>Soap pyrolysis is an interesting route for green jet fuel production because its 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 density and viscosity of bio-oil product. The bio-oil composition produced from thermal process are olefins C₆-C₁₈ (43.4%), ketones (38.6%), and paraffins C₇-C₁₈ (14.8%). Thermal pyrolysis showed low yield bio-hydrocarbon (olefins and paraffins) C₈-C₁₆ (11%) and high solid residual formation (23.4%). Catalytic pyrolysis using zeolites reduced solid residual formation to 10.6% with high bio-oil yield, however, the undesired carboxylic acid products was 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. Main products of pyrolysis bio-oil over H-M are olefins C₆-C₁₈ (48.9%), ketones (24.5%), and paraffins C₇-C₁₈ (15.9%). The range of bio-hydrocarbon produced was mainly similar with jet fuel. Catalytic pyrolysis route using zeolites improved quality of bio-oil and reduced coke formation.</p>	
Response to Reviewers:	Response to Reviewer Comments	

Reviewer #1: Catalytic Pyrolysis of Coconut Oil Soap using Zeolites for Bio-hydrocarbon [BCAB-D-21-00404] Production. The manuscript highlights the catalytic pyrolysis of soap in a batch reactor. Below are some points which would help in formatting the manuscript for BCAB:

Comment 1:

1. Page 3, line 30 to 33 use bio oil or bio-oil or bio-hydrocarbon or oil. This must be corrected in the entire manuscript.

Response 1:

The manuscript has been revised. We use the term bio-oil for the oil produced from the soap pyrolysis. We also use the term bio-hydrocarbon which comprise of olefins and paraffins to make the reader aware of the hydrocarbon.

Comment 2:

2. Page 4, line 24 to 25, space before reference.

Response 2:

The manuscript has been revised.

3. Page 5, table 1, replace P and T with pressure and temperature. Assign equation number.

Response 3:

The manuscript has been revised. Please refers to Table 1

4. Page 7, line 4 to 5, space before reference.

Response 4:

The manuscript has been revised.

5. The reference style or bibliography in the entire manuscript should be carefully placed through reference software.

Response 5:

The manuscript has been revised.

6. Try to justify the result of GC Ms by FTIR or ¹H NMR.

Response 6:

Thank you for your advice. We would consider for FTIR analysis in future investigation

7. The hydrocarbon product from the pyrolysis zone should have been tested for changes in calorific values.

Response 7:

Thank you for your suggestions. We would like to consider it in future work.

8. The impact of inhibited elements on the catalysts during pyrolysis was not studied.

Response 8:

Thank you for your advice. The impact of inhibited elements on the catalysts during were out of the investigation scope. We would like to consider it in future work.

9. The coke formed after pyrolysis must be analysed for the deposition of elements and tar.

Response 9:

There were several studies study the coke elemental composition and tar. We added literature discussions to improve our manuscript. Please refers to section 3.1 the last paragraph.

Reviewer #2: 1. The definition of coconut oil soap as a raw material must be explained, where it is obtained

Response 1:

Please refers to section 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. The operating pyrolysis temperature has not been described. How does the reactor

work?

Response 2:
The manuscript has been revised. Please refers to Section 2.3 the second paragraph.

3. Usually in biomass pyrolysis will be formed aldehyde, aromatic, alcohol etc. What about the observations of this research, why were only olefins, ketones and paraffins identified?

Response 3:
We obtain those products and put in the “other” in the first version of the manuscript. We explain the products in the revised version. Please refers to Section 3.1 and Section 3.3.

4. Overall, the pyrolysis process and data collection have not been conveyed well.

Response 4:
The manuscript has been revised.

5. Which are the optimum conditions with the best results?

Response 5:
Actually, we did not perform the optimization research. However, we can say that the mordenite catalyst is promising to investigate more.

6. the keyword green jet fuel was not found in the abstract

Response 6:
The manuscript has been revised. Please refers to abstract in the first sentence.

7. What about the characteristics of raw materials, ultimate analysis, proximate, etc.?

Response 7:
The characteristics of raw materials, ultimate analysis, proximate was not performed in this work. We focus on the product yield and selectivity of components by using different loading and type of zeolites.

8. The characteristics of each catalyst are shown in the table, If possible display SEM results

Response 8:
The manuscript has been revised. Please refers to Table 2 for the zeolite properties. We did not perform the SEM analysis.

9. The method of research is less clear, describe it better

Response 9:
The manuscript has been revised. Please refers to part 2. Experimental Section.

10. There is no explanation for how to research, add clearly.

The manuscript has been revised. Please refers to part 2. Experimental Section.

How do you calculate the total composition of the product, biooil, gas and coke?

Response 10:
Please refers to Section 2.4. Product yield was calculated based on mass weigh of each product (bio-oil, coke) divided by total initial mass of soap, except for gas which was not weighed. The yield of gas was determined by mass balance.

11. What table is the yield product data obtained?

There is no product yield research data

Response 11:
The yield products data are presented in Figure 4 and Figure 9. The percentage of each product is mentioned in the Figures. Please refers to those figures.

12. Check the equation again, reference sources?

Response 12:
The reference has been added. Please refers to equation 1.

13. a. How to calculate the percent oxygenate, paraffin and olefins?

Response 13a:
Bio-oil components were analysed by using GC-MS. The percent oxygenate, paraffin,

and olefins calculated by % area of each peak appeared in chromatogram divided by total area.

b. Is there no other components such as aromatic, aldehyde, alcohol, etc.?

Response 13b:

Yes, we observed those components in the bio-oil products in small quantities. We revised the manuscript to make clear the impurities components detected. Please refers to Section 3.1 paragraph before Table 3.

14. At 3.5. It is not clear what that means. What is the relationship between the type of catalyst, the amount with the physical properties obtained, explain?

Response 14:

The bio-oil products physical properties depend on its components. We observed that the bio-oil product resulted from pyrolysis using H-Y contain high carboxylic acids, particularly with sample loading 0.6. The density of carboxylic acid is 0.88 g/mL higher than the paraffinic/olefinic with density average 0.75 g/mL which contributed to make the density of bio-oil from pyrolysis using H-Y high.

15. The conclusion does not include quantitative results which are the optimum conditions and the best results?

The conclusions have not yet culminated in a good conclusion

Response 15:

In this study, we investigated the effect of zeolite loading and the type of zeolites. The optimization part will be conducted in the next works. Thank you for your suggestion.

16. Reference is still lacking, include the results of research in 2021

Response 16:

The manuscript has been revised. We cited recent published articles in 2021.

Reviewer #4: Catalytic Pyrolysis of Coconut Oil Soap using Zeolites for Bio-hydrocarbon Production

BCAB-D-21-00404

Comments:

This manuscript demonstrates the use of zeolite to catalyze pyrolysis of coconut oil soap to produce bio-hydrocarbon, by adjusting the type of zeolite (H-Y and H-M) and the loading of H-Y to improve the quality of bio-oil and reduce the formation of coke. Based on the research results of this manuscript, it seems that H-M is more suitable for producing bio-hydrocarbon and reducing coke yield than H-Y. However, due to the lack of reasonable characterization results, it is difficult to understand the structure-activity relationship of these two catalysts to pyrolysis of coconut oil soap. Experiments have showed that loading 20% of H-Y obtains the highest hydrocarbon yield. Why should the loading of H-M choose 40%? Moreover, the effect of the loading of H-M with better catalytic performance on the pyrolysis properties of coconut oil soap has not been discussed. Therefore, due to the lack of scientific significance and innovation of this manuscript, it is difficult to publish it in Biomass Conversion and Biorefinery with the current quality.

General Response:

The manuscript has been improved. Hopefully, it meets the standard quality to be published in Biomass Conversion and Biorefinery

1. In the abstract section, the authors briefly clarify the purpose, experimental program and main conclusions of this study. However, the method to reduce the formation of coke is vague. Is it through the use of a batch reactor or the addition of a catalyst? In

addition, "bio-oil" is a more general writing.

Response 1:

The abstract has been revised. The coke formation was reduced because of using catalyst. The batch reactor was removed from the sentence. We used bio-oil for the whole article.

2. The introduction section is confusing, and it is difficult to find out the significance of the work done in this manuscript for this research field. The second and third paragraphs are used to summarize the influence of different feedstocks, technical routes and operating parameters on pyrolysis plant/animal oil. This has almost nothing to do with this research, but it takes a considerable amount of space to introduce it. Please focus on introducing the current application status of catalysts in the catalytic pyrolysis of oil soaps.

Response 2:

Please refers to paragraph 4-6 to find the current application status of catalysts in the catalytic pyrolysis of oil soaps.

3. "Catalytic pyrolysis over H-Y zeolite reduced the coke formation." is written in part 3.1, please give a more detailed explanation.

Response 3:

The manuscript has been revised. Please refers to part 3.1

4. Figure 5 shows the used catalyst, and simply judged by the color of the solid residue that an increase of the loading can reduce the formation of solid. Although the method of judgment is simple, it seems irrational. The yield of coke is clearly given in Figure 4a, please explain its calculation method. In addition, the article stated that the formation of aromatic hydrocarbons has the same trend as the formation of coke.

Response 4a:

The coke yield was calculated according to equation below

$$\text{coke} = (\text{mass of solid residual} - \text{mass of zeolite}) / (\text{mass of soap input}) \times 100\%$$

There are several indications that the coke decreased in the pyrolysis over zeolite.

The decreasing of solid residual mass

Change of solid colour from black in the thermal pyrolysis to brighten over H-Y 0.6

The bio-oil and water yield from pyrolysis using zeolite also increase significantly which suggested that shifting product selectivity from coke to bio-oil

Why are there no aromatic hydrocarbons in the bio-oil components in this study?

Response 4b:

We found aromatic hydrocarbons as trace element. The manuscript has been revised.

5. After adding the catalyst H-Y in part 3.2, the selectivity of hydrocarbons decreased and accompanied by an increase in carboxylic acid products. However, acid products usually cause the pH of bio-oil to decrease, making it corrosive. On the whole, adding H-Y catalyst is not conducive to improving the quality of bio-oil.

Response 5:

Yes, the catalyst H-Y is not recommended because of high carboxylic acid in the bio-oil product. The carboxylic acids products, mainly lauric acid and myristic acid, increased in bio-oil when using zeolite H-Y during pyrolysis (Figure 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 was 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 sodium soap and the protonated zeolite H-Y (equation 2). The more H⁺ provided by zeolites the more carboxylic acids formed.

6. The concepts of coke and char seem to be blurred in this manuscript.

Response 6:

According to Du et.al (2013), char and coke are different depending the mechanisms and in which part the carbon was formed. Char was formed on the wall of pyrolysis reactor and the external surface of catalysts and coke was formed in the micropore of catalysts [1]. However, in our study the char and coke were lumped as coke. The manuscript has been revised. Please refers to introduction section

7. Part 3.3 is difficult to understand. First, please give the NH₃-TPD results of the two catalysts. Secondly, please explain the relationship between the type of acid sites and the formation of coke more rationally. In addition, the two catalysts have different pore sizes and extremely different BET surface areas. What impact will this have on the difference in catalytic performance of the two catalysts?

Response 7:

We did not perform the NH₃-TPD of the catalysts. However, we did in previous work for the MOR catalyst which showed that the strong acid sites observed [2]. The high ratio of Si/Al suggested that the number acid sites of H-MOR were lower than H-Y. Despite the number of acid sites of H-MOR was lower than H-Y, strong acid sites of H-M was probably much higher than H-Y, hence reduce coke production.

8. If the physical properties of jet fuel can be provided for comparison, it may be more helpful to illustrate the effect of zeolite type and loading.

Response 8:

The properties of jet fuel A-1 has been incorporated in the manuscript according to literature [3]. Please refers to Table 7.

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 fractionation distillation to meet commercial Jet A-1 requirement as presented in Figure 1

Some minor issues:

1. Please check the table number carefully. There are two Table 2 in the current manuscript.

Response 1 minor issues:

The manuscript has been revised

2. Please check the format of the reference. For example, page 4, line 56; references 18 and 20.

Response 1 minor issues:

The manuscript has been revised.

References

1. 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. <https://doi.org/10.1039/C3GC41581C>
2. Kurniawan T, Muraza O, Hakeem AS, et al (2017) Selective Isomerization of n-Butane over Mordenite Nanoparticles Fabricated by a Sequential Ball Milling-Recrystallization-Dealumination Route. *Energy and Fuels* 31:. <https://doi.org/10.1021/acs.energyfuels.7b02555>
3. (2000) Handbook of Products. Air BP, Hertfordshire, United Kingdom

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Catalytic Pyrolysis of Coconut Oil Soap using Zeolites for Bio-hydrocarbon Production

^aTeguh Kurniawan*, ^aAchmad Setiawan, ^aNurika Andana Putri, ^aAnton Irawan, ^bAsep Bayu Dani Nandiyanto, ^cYazid Bindar

^aChemical Engineering Department, Universitas Sultan Ageng Tirtayasa, Serang 42122, Indonesia

^bDepartment of Chemistry, Universitas Pendidikan Indonesia, Bandung, 40154, Indonesia

^cInstitut Teknologi Bandung, Chemical Engineering, Bandung 40116, Indonesia

*Email: teguh@untirta.ac.id

Abstract

Soap pyrolysis is an interesting route for **green jet fuel** production because its 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 density and viscosity of **bio-oil** product. The **bio-oil** composition produced from thermal process are olefins C₆-C₁₈ (43.4%), ketones (38.6%), and paraffins C₇-C₁₈ (14.8%). Thermal pyrolysis showed low yield **bio-hydrocarbon (olefins and paraffins)** C₈-C₁₆ (11%) and high solid residual formation (23.4%). Catalytic pyrolysis using zeolites reduced solid residual formation to 10.6% with high **bio-oil** yield, however, the undesired carboxylic acid products was 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. Main products of pyrolysis **bio-oil** over H-M are olefins C₆-C₁₈ (48.9%), ketones (24.5%), and paraffins C₇-C₁₈ (15.9%). The range of bio-hydrocarbon produced was mainly similar with jet fuel. Catalytic pyrolysis route using zeolites improved quality of bio-oil and reduced coke formation.

Keywords: Pyrolysis, zeolite, coconut oil soap, bio-hydrocarbon, green jet fuel, coke

1
2 **1. INTRODUCTION**
3

4 Fossil fuel depletion is unavoidable due to its nature as a non-renewable material while it
5 consumes continuously since the industrialization era. The emission of greenhouse gasses from
6 combustion of fossil fuel is the main contributor to the global warming. Transportation sectors
7 depend heavily on the fossil fuel. For example aviation industry fuel consumption reached 1.4
8 million barrels per day in US in the beginning year of 2020 [1]. Electric car is currently become
9 trend to substitute the conventional fossil fuelled car, however the electric aircraft is still need
10 time before ready to be commercialized. Electric aircraft commercialization is restricted with
11 current status of battery with specific energy only 200 Wh/kg which means 1.7% of the jet fuel
12 energy content [2]. Low specific energy of battery becomes the main obstacle to use electric
13 aircraft in near futures. Hence, green fuel from renewable sources would be potential
14 alternative to substitute fossil fuel before the electric aircraft technology commercially
15 applicable.
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36 Various feedstocks could be employed for bio-hydrocarbon production such as plant/animal
37 oil, lignocellulosic biomass, sugar rich material, and solid fraction of municipal solid waste [3].
38 Plant or animal oil are among potential feedstocks for green fuel production. Several process
39 technologies routes have been developed to produce green jet fuel from plant/animal oil such
40 as transesterification, direct pyrolysis, hydrodeoxygenation (HDO) and soap pyrolysis [4][5].
41 Commercial technology using HDO requires hydrogen which is expensive and need high
42 pressure operation. Simple process technology such as soap pyrolysis was established during
43 the Second World War in China to produce gasoline and diesel oil from tung oil soap [6].
44 Process block diagram of soap pyrolysis is presented in Figure 1. Saponification of vegetable
45 oil with basic solution followed by pyrolysis produced bio-oil which then is distilled into
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1 gasoline, jet fuel and diesel oil. The soap pyrolysis route is rather simple process, i.e., operated
2 under atmospheric pressure operation and no hydrogen requirement, instead of other
3 complicated routes to produce bio-hydrocarbon fuel.
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9 Table 1 presents literature survey in soap pyrolysis to produce bio-hydrocarbon. Temperature
10 operating of pyrolysis affects the yield of pyrolysate products, particularly residual solid yield
11 i.e. salt and coke. According to Du et.al, char and coke are different depending the mechanisms
12 and in which part the carbon formed. Char is formed as macromolecules on the wall of
13 pyrolysis reactor and the external surface of catalysts, while coke is formed in the micropore
14 of catalysts [7][8]. Pyrolysis soap at low temperature 150-300 °C produced high amount of
15 residue 37-78%, while at high temperature 400 °C residue is only 5.5% [9]. Solid residues yield
16 was also reported high in thermal pyrolysis of palm stearine soap at temperature 370 °C with
17 residual solid yield in the range of 44-57% [10]. Feedstocks soap types were also reported
18 affected the products yield [11]. Pyrolysis of calcium salts of tung oil was produced more
19 residual coke (48.6%) and low yield bio-oil product (41.5%) than pyrolysis of calcium salts of
20 stearic acid with residual coke only 17.3% and high yield oil product 76%. Tung oil consists
21 of about 80% eleostearic acid ($C_{18}H_{30}O_2$) which has three conjugated double bonds while the
22 stearic acid ($C_{18}H_{36}O_2$) is saturated fatty acids type. The three conjugated double bonds
23 favoured cyclization process to produce aromatic which led further reaction into coke.
24 Feedstock selection was crucial to obtain high yield of bio-hydrocarbon in the bio-oil products.
25 Lappi and Allen reported that pyrolysis of castor oil soap which is rich in ricinoleic acid
26 ($C_{18}H_{34}O_3$) with hydroxy fatty acid, resulted in high ketone and aldehyde of bio-oil pyrolysate,
27 while pyrolysis of palm oil soap rich in palmitic acid produced high paraffin and olefin
28 component with low oxygenates compound [12].
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Catalysts for soap pyrolysis is important to increase the reaction rate and improve product selectivity. Metals of soap has important role as catalysts as reported in the literature [13][10]. Mg-Fe catalyst was found to be effective in suppressing alkene production which has negative effect on stability of green diesel produced [13]. Metal oxide such as ZnO acted as active catalyst in the isomerization to produced iso-paraffin from palm stearine [10]. Cement which mainly consist of CaO and Al₂O₃ was reported as catalyst for sodium palm oil soap pyrolysis which was reported reduce the oxygenated compound in the pyrolysate [9].

Table 1. Literature survey of pyrolysis oil soap investigations

Catalysts added	Metals Cation	Soap types oil sources	Ratio Catalyst to Soap	Reactor type/ material	Pressure atm	Temperature (°C)	Time (min)	% wt.				% oil yield*	Ref.
								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	[11]
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	[11]
Cement (CaO & Al ₂ O ₃ dominant)	Na	Palmitic soap	30:70	Batch with electric heater/ stainless steel	1	T room - 300	75	7.2	22.6	28	37.8	31.7	[9]
Cement (CaO & Al ₂ O ₃ dominant)	Na	Palmitic soap	30:70	Batch with electric heater/ stainless steel	1	T room - 400	75	7.0	21.0	63	5.5	70.4	[9]
No	Mg-Fe	Palm stearin	0	Batch /glass reactor	1	350	360	6.7	7.5	47.5	38.4	50.9	[13]
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	[14]

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

1 Zeolites are microporous crystalline materials which is well-known catalysts in refinery and
2 petrochemical industries. Zeolite Y is among the most important catalyst in oil cracking to
3 produce alkane, alkene, and cycloalkane. Zeolites are also found in nature in massive amount,
4 hence the price is cheap as compared with the synthetic zeolites. Commercial application of
5 natural zeolites for industrial catalyst was in the selectoforming process developed by Mobil
6 Oil for removal low octane normal alkanes by selective hydrocracking on erionite containing
7 about one tenth percent platinum [15]. Pyrolysis of lignin was studied by Lee et. al. using
8 natural zeolites in the pyrolysis reactor and fed into the bed of H-ZSM-5 in the sequential
9 reactor. The series reactor configuration has decreased the coke deposition in the expensive
10 HZSM-5 and improved the product oil quality [16].
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26 Catalytic pyrolysis soap to produce bio-hydrocarbon using zeolites are rarely reported. We
27 investigated pyrolysis of coconut oil soap using zeolites to synthesize green jet fuel using
28 zeolites as catalyst. Effect of catalyst zeolites loading, zeolite type to product yield and
29 properties were further studied. The main originalities of this studies are utilization zeolites,
30 i.e., FAU and MOR, catalysts to reduce coke yield and improve bio-oil quality.
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41 **2. EXPERIMENTAL SECTION**

42 The research was designed to study the effect of zeolite types, i.e., H-Y and H-MOR. The effect
43 of zeolite loading was also investigated for sample H-Y with loading 0.2, 0.4, and 0.6 g.
44 Catalyst preparation was conducted by ion-exchange method followed by drying and
45 calcination. The catalysts were tested for soap pyrolysis. The detailed procedures are presented
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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 Catalysts 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 m²/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 m²/g and Si/Al = 4.4[17]. The zeolites were ion-exchanged with 2 M NH₄NO₃ 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 oven at 110 °C. The dried zeolites were calcined in furnace at 550 °C for 8 h to obtain protonated zeolites. The samples were labelled H-Y and H-M for protonated zeolite Y and protonated natural mordenite, respectively.

2.3 Catalysts Evaluation

The protonated zeolites were tested by using pyrolysis reactor under atmospheric pressure. The experimental setup presented in Figure 2 consists of heater, reactor, and condenser. The weight ratio of H-Y to soap were varied 0, 0.2, 0.4 and 0.6. Zeolite mordenite (H-M) was also tested at ratio H-M to soap 0.4.

1 The soap and catalyst with certain ratio were loaded into the pyrolysis reactor. Heater was
2 turned on and temperature operation in pyrolysis reactor is maintained to follow curve started
3 from ambient temperature to 312 °C as presented in Figure 3. Pyrolysis was performed under
4 autonomous pressure. After 20 min, the heater was turned off while the condenser maintained
5 on until the pyrolysis reactor temperature dropped to ambient temperature. Products of coconut
6 oil soap pyrolysis were water, bio-oil, gas, and solid residue (salt, catalyst, char and coke). All
7 of the products were weighed, except the gas which was determined by mass balance
8 calculation. In this study char and coke were lumped as coke.
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22 **2.4 Products Analysis**

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24 We analysed bio-oil products both physical and chemicals properties. Physical analysis was
25 performed using pycnometer, viscometer Cannon-Fenske for density and viscosity analysis,
26 respectively. Specific gravity and API gravity determined based on density and viscosity data.
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28 A gas chromatography mass spectrometry (GC-MS, GCMS-QP2010 Ultra, Shimadzu Corp.,
29 Japan) was used to determine products component identification and composition. **Product**
30 **yield was calculated based on mass weigh of each product (bio-oil, coke) divided by total initial**
31 **mass of soap.**
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44 **3. RESULTS AND DISCUSSION**

45 **3.1 Effect of Catalyst Zeolite H-Y Loading on Products Yield**

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47 Figure 4a presents effect of catalyst zeolite H-Y loading on product yield. Soap pyrolysis
48 without catalyst zeolite shows the highest solid residual yield 23.4%. On the other hand,
49 pyrolysis with H-Y loading 60% shows the lowest solid residual yield 12.4%. Solid residual
50 most likely consisted of Na₂CO₃, coke, and unconverted soap. **Catalytic pyrolysis over H-Y**
51 **zeolite reduced the coke formation. There were several indications that coke reduced over H-**
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Y i.e. a) The decreasing of solid residual mass. Change of solid colour from black in the thermal pyrolysis to brighten over H-Y 0.6; (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 [13]. Pyrolysis temperature in this work was lower (room temperature-312 °C) than reported in literature which was 350-400 °C. Probably, sodium soap more active as catalyst for decarbonylation and decarboxylation 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 Na₂CO₃ formation from coconut oil soap which is mainly sodium lauric acid was possibly follows equation 1 below.

The equation was modified from literature reported elsewhere [19].

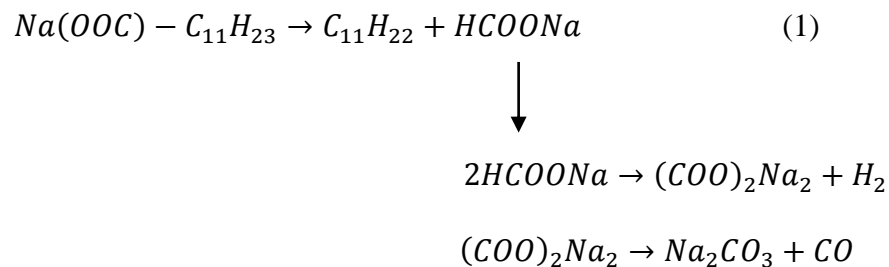


Figure 4b presents composition of bio-oil product. It is seen clearly that olefins are the main component of bio-oil for all experiments. The metal of sodium in the soap feedstock most likely controlled the selectivity to olefins as seen in equation 1. Olefins as major product was also reported by another group that used sodium metal soap as feedstock [12][19]. Paraffin was reported as the main hydrocarbon products instead of olefins when used metal alkaline earth soaps such as calcium and magnesium soap as the feedstock [10][13]. The impurities products (written as other in Figure 4b) in the bio-oil for pyrolysis without zeolites was identified such

as 1-undecanol, oleyl alcohol, and azulene. For pyrolysis using zeolites 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.

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 (<i>Cocos nucifera</i>)	Na/H-MOR	16	49	35	GC-MS	This work
Macauba oil (<i>Acrocomia sclerocarpa</i>)	Ca	37	42	21	GC-MS	[20]
Palm stearin (<i>Elaeis guineensis</i>)	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 (<i>Elaeis guineensis</i>)	Mg-Fe	94	6	Not reported	GC-FID with standard alkane for calibration	[13]
Palm oil (<i>Elaeis guineensis</i>)	Na	14	40	6	GC-MS	[12]
Castor oil (<i>Ricinus communis</i>)	Na	6	8	45	GC-MS	[12]
Palm oil (<i>Elaeis guineensis</i>)	Na/CaO-Al ₂ O ₃	41	13	17	GC-MS	[9]

Figure 5 presents 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. The higher loading of H-Y the darkness levels of solid residue reduced significantly. Coke was formed through condensation mechanism as reported elsewhere [11]. Aromatic hydrocarbons cracked produce 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

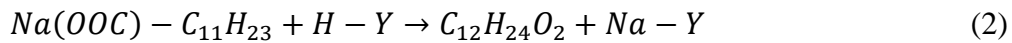
1 was reported produce more aromatic instead of calcium soap of stearic acid, as the results the
2 coke formation of tung oil soap pyrolysis was higher than the stearic acid soap. Zeolite with its
3 acid sites most likely inhibited coke formation through cracking mechanism of the long
4 hydrocarbon chain. H-Y was reported as active catalyst for cracking vacuum gas oil (VGO)
5 with high conversion into gasoline diesel oil, kerosene, lighter component, and coke [21]. The
6 high conversion of VGO over H-Y was attributed to its high acid site density.
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17 Perigolo et. al. investigated coke formed from pyrolysis oleic acid soap oxidized at relatively
18 low temperature range 300-500 °C which suggested that the coke contained reactive defective
19 carbon [18]. Char was formed largely in low temperature range 150-300 °C and decrease as
20 temperature of pyrolysis increased as reported by Hussain et.al. [9]. Char/coke derived from
21 biomass pyrolysis was polyaromatics with carbonyl and hydroxyl end groups as indicated by
22 the FTIR and Raman analyses through aldol and Diels-Alder mechanism [7].
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34 **3.2 Effect of Catalyst Zeolite H-Y Loading on Bio-hydrocarbon Selectivity**

35 Coconut oil main fatty acid composition was 47% lauric acid ($C_{12}H_{24}O_2$) as presented in [Table](#)
36 [4](#) [22]. The main component of bio-hydrocarbon product was 1-undecene ($C_{11}H_{22}$) which was
37 most likely formed from the main sodium salt fatty acid component of coconut oil (lauric acid)
38 through the homolysis of the weakest C–C bond next to the carboxylic group [12][23]. The
39 [bio-oil](#) yield increase and the coke formation reduced over zeolite H-Y, however, the
40 chromatogram area under the peaks of bio-hydrocarbon slightly decrease as seen in [Figure 6](#)
41 and [Figure 7](#). Despite the bio-hydrocarbon percentage in the [bio-oil](#) over zeolite H-Y were
42 lower than without zeolite the bio-hydrocarbon yield was still high. Here, the bio-hydrocarbon
43 yield is oil yield multiply by the selectivity.
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1 The carboxylic acids products, mainly lauric acid and myristic acid, increased in bio-oil when
2 using zeolite H-Y during pyrolysis (Figure 6 highlighted in red and yellow). The carboxylic
3 acids products were not significantly detected in thermal pyrolysis without zeolite H-Y. The
4 higher H-Y loading, the more carboxylic acids produced. Carboxylic acids formed was 6.8%
5 at H-Y loading 0.2 and increased to 19.7% at H-Y loading 0.6. The lauric acid product is most
6 likely formed because of hydrogen transfer between the sodium soap and the protonated zeolite
7 H-Y (equation 2). The more H⁺ provided by zeolites the more carboxylic acids formed.
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24 Bio-hydrocarbon produced via soap pyrolysis route was similar with fossil-based hydrocarbon
25 components such as gasoline(C₄-C₁₂), diesel oil (C₁₂-C₂₀), and jet fuel (C₈-C₁₆) as seen in
26 Figure 8. Jet fuel range was the dominant fuel produced from pyrolysis of coconut soap. Lauric
27 (C₁₂:0) and myristic acid (C₁₄:0) as dominant fatty acids in coconut oil with 47% and 18%,
28 respectively, determined product of bio-hydrocarbon that resulted from its homologous carbon
29 range. HY-loading 0.2 shows the highest bio-oil yield among others.
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41 **3.3 Effect of Zeolites Type on Products Yield**

42 Yield of solid residue over H-M was significantly low (ca. 10.6%) as compared with H-Y (ca.
43 17%) as seen in Figure 9a. Surface area of zeolite-Y, 650 m²/g, was higher than the natural
44 zeolites with 19 m²/g. Theoretical pore diameter of zeolite Y is 7.4 Å with three-dimensional
45 pore structure, while mordenite is 6.7 Å and one-dimensional pore structure only. From textural
46 properties perspective, zeolite Y has superiority instead of mordenite. One may expect that the
47 coke residue over H-Y lower than mordenite. However, the results showed that solid residue
48 of coconut oil soap pyrolysis over H-Y was higher than H-M. It is most likely the acid sites of
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1 zeolites control the coke yield. From our previous work [24], TPD ammonia results of MOR
2 showed two buds, one in lower temperature range and the other in higher temperature range
3 which indicated low and strong acid sites, respectively. Comparison of acidity H-Y with Si/Al
4 5 and H-MOR 10 with Si/Al suggested that H-M showed number of strong acid sites higher
5 than H-Y [25]. In present work, zeolite H-MOR Si/Al was 4.4 and H-Y was 2.6. The high ratio
6 of Si/Al suggested that the number acid sites of H-MOR were lower than H-Y. Despite the
7 number of acid sites of H-MOR was lower than H-Y, strong acid sites of H-M was probably
8 much higher than H-Y, hence reduce coke production.
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22 Carboxylic acid formation was pronounced over H-Y zeolite with 18.9% instead of H-M
23 zeolite with only 2.9% (Figure 9b and Figure 10). It is most likely because ratio of Si/Al of H-
24 Y is lower than H-M which means H-Y has high acid density. As the result the H^+ available in
25 H-Y much higher than H-M for H^+ transfer reaction in equation 2 producing more carboxylic
26 acids. Ketone formation in bio-oil from pyrolysis over H-M was the lowest as compared with
27 H-Y and without zeolites (Figure 9b). According to Hsu et.al., ketone was produced from
28 splitting off carbon monoxide from the metals fatty acids [11]. Paraffin and olefins product
29 from soap pyrolysis over H-M shows higher percentage than H-Y and without zeolite.
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44 **3.4 Effect of Zeolites Type on Bio-hydrocarbon Selectivity**

45 Figure 11 present effect of zeolites type on paraffins and olefins composition. Paraffinic
46 products detected for all samples were from C_7 to C_{18} with main components C_{11} and C_9 . The
47 percent composition of C_9H_{20} was the highest over H-M zeolite, while $C_{11}H_{24}$ was the highest
48 on the thermal pyrolysis without zeolite. It is possibly that the cracking of long chain carbon
49 occurred over H-M because of its strong acid sites. Olefinic products were detected within the
50 range of C_6 to C_{18} with main product C_{11} . The percent composition of $C_{11}H_{22}$ was the highest
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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 effect of zeolites type on green fuel production. Pyrolysis of soap over H-M shows its superiority both in oil yield and bio-hydrocarbon composition, 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, low acid site density was suitable to reduce coke formation and improve the green fuel yield. The low-cost of natural mordenite and extensive availability give 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 [10][13].

3.5 Effect of Zeolites 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 increasing 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

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pyrolysis over H-M contain more bio-hydrocarbon C₆-C₁₈ (paraffins and olefins) and low oxygenated compound C₁₂-C₃₁ (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 fractionation distillation to meet commercial Jet A-1 requirement as presented in Figure 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 oxygenates compound. Bio-hydrocarbon produced consisted of olefins and paraffins with carbon chain length C₆-C₁₈ which are potential to substitute conventional jet fuel. The solid residual yield was decrease along with the increasing of zeolites loading, however, the bio-oil component of carboxylic acid was increase. The combination uses of other metals soap instead of sodium and zeolites with various cations or impregnated metals, type, crystal size, acidity could be interested to investigate in order to reduce oxygenate compounds and shifted olefinic products to more paraffins.

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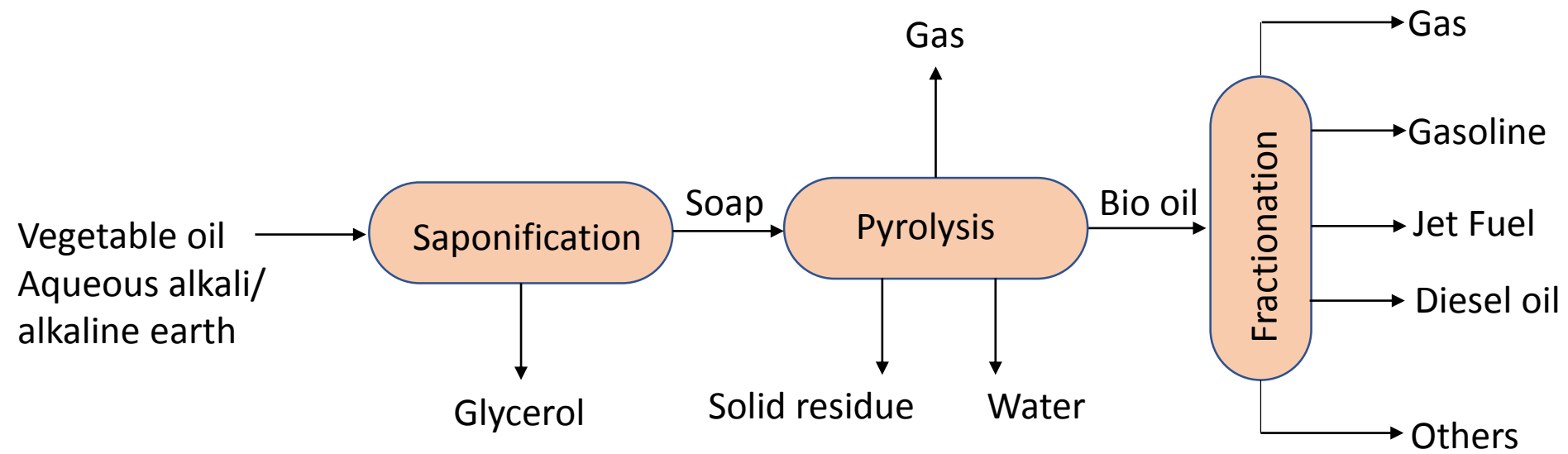


Figure 1. Flow diagram of metal soap pyrolysis into green fuel.

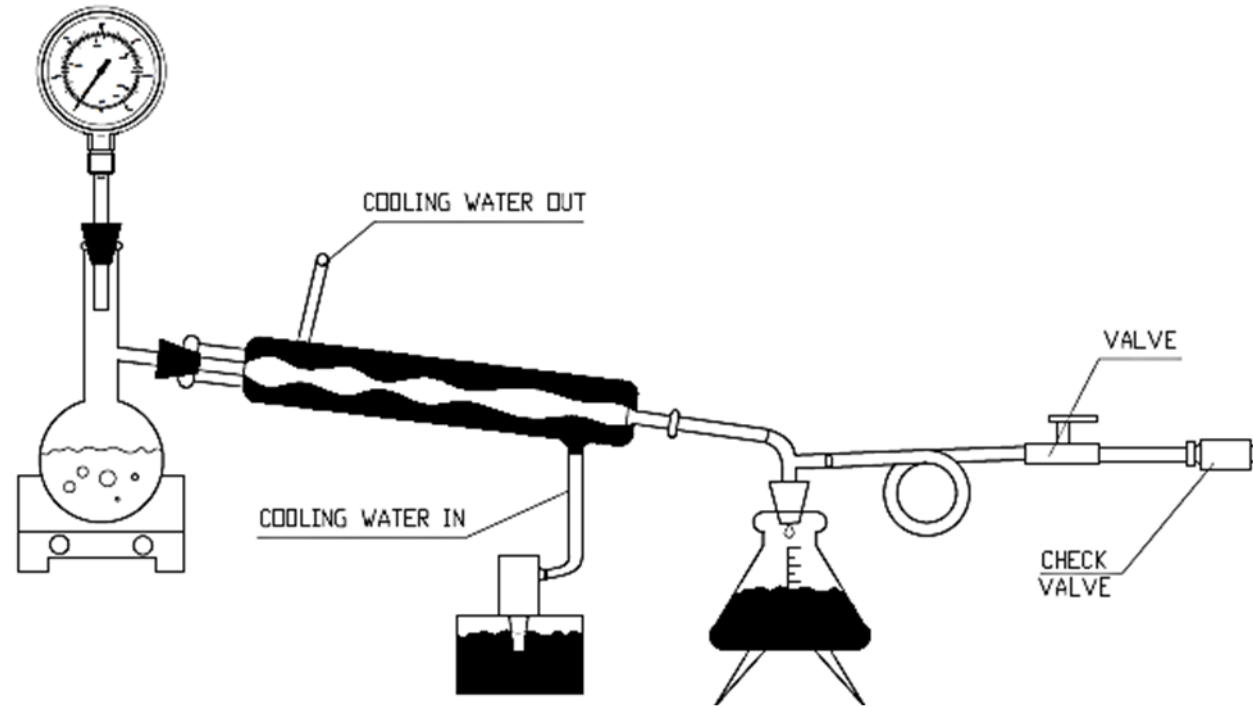


Figure 2. Schematic reactor for soap pyrolysis.

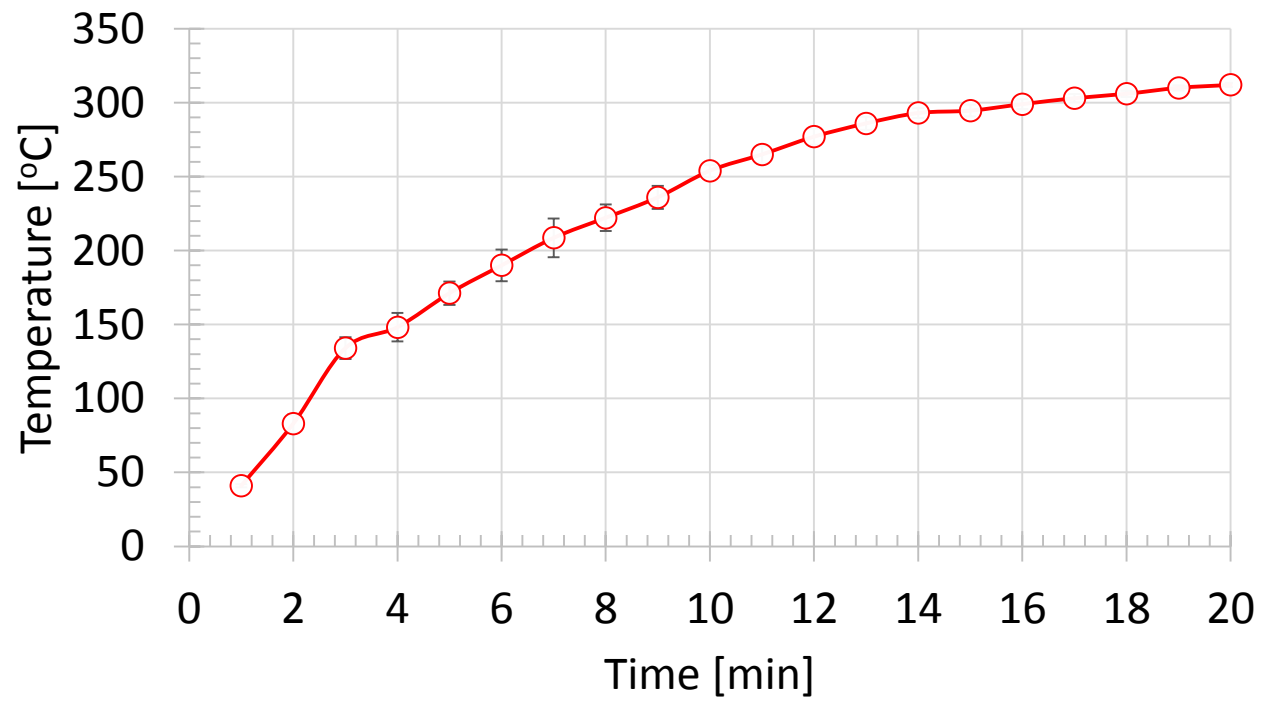


Figure 3. Pyrolysis temperature curve.

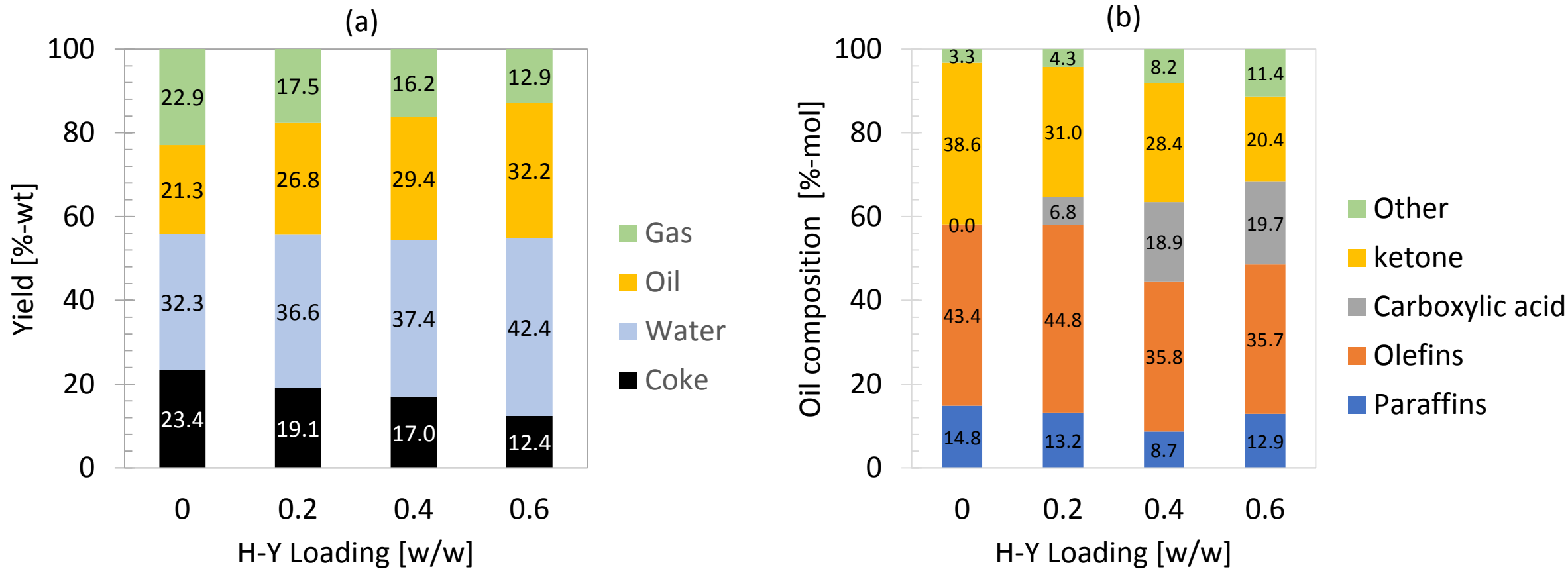


Figure 4. Effect of catalyst zeolite H-Y loading on (a) products yield and (b) oil composition.



(a) No catalyst



(b) HY-0.2



(c) HY-0.4



(d) HY-0.6

Figure 5. Spent catalyst of H-Y zeolite mixed with solid residues after soap pyrolysis.

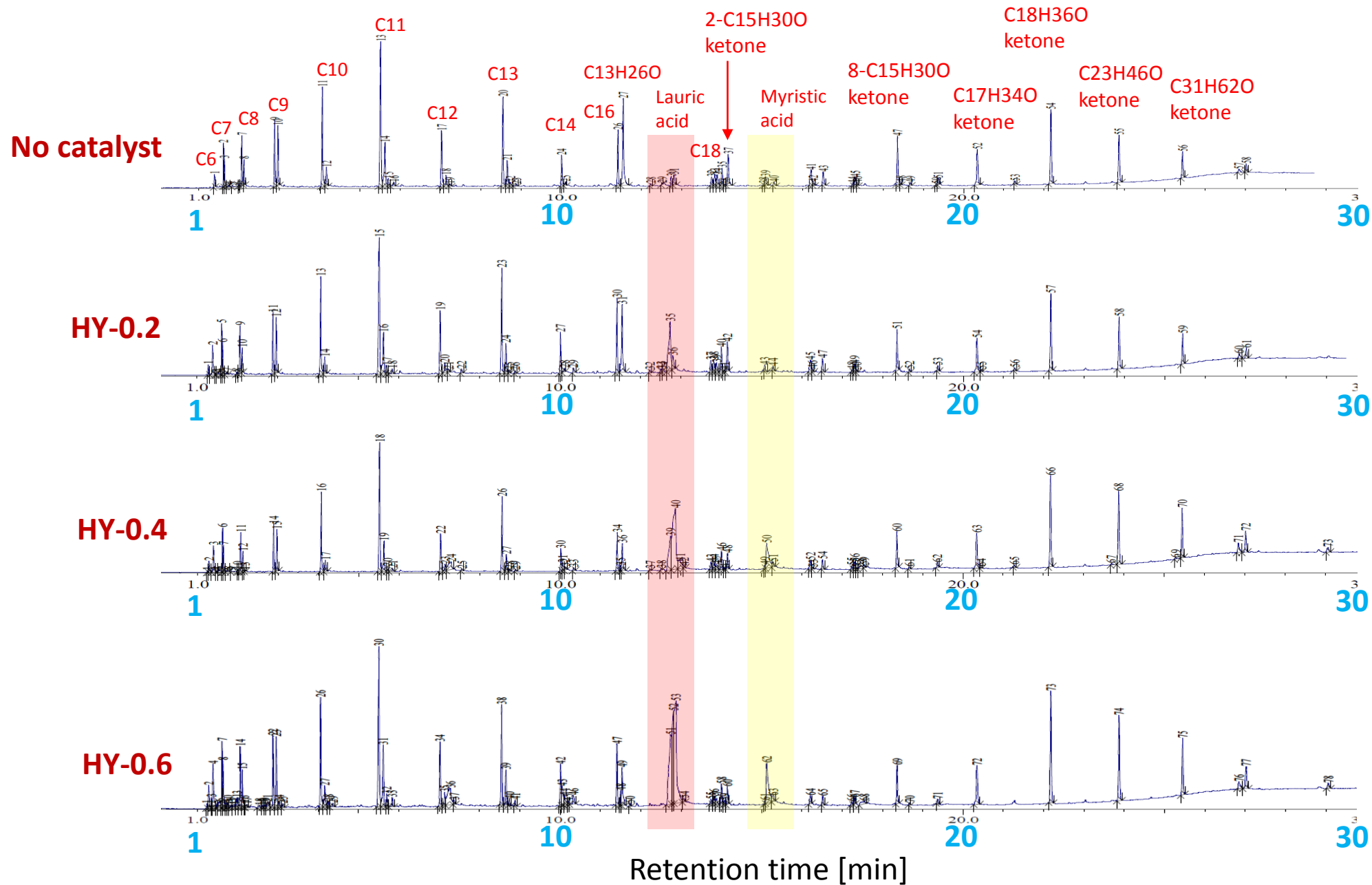


Figure 6. Effect of catalyst loading on products composition.

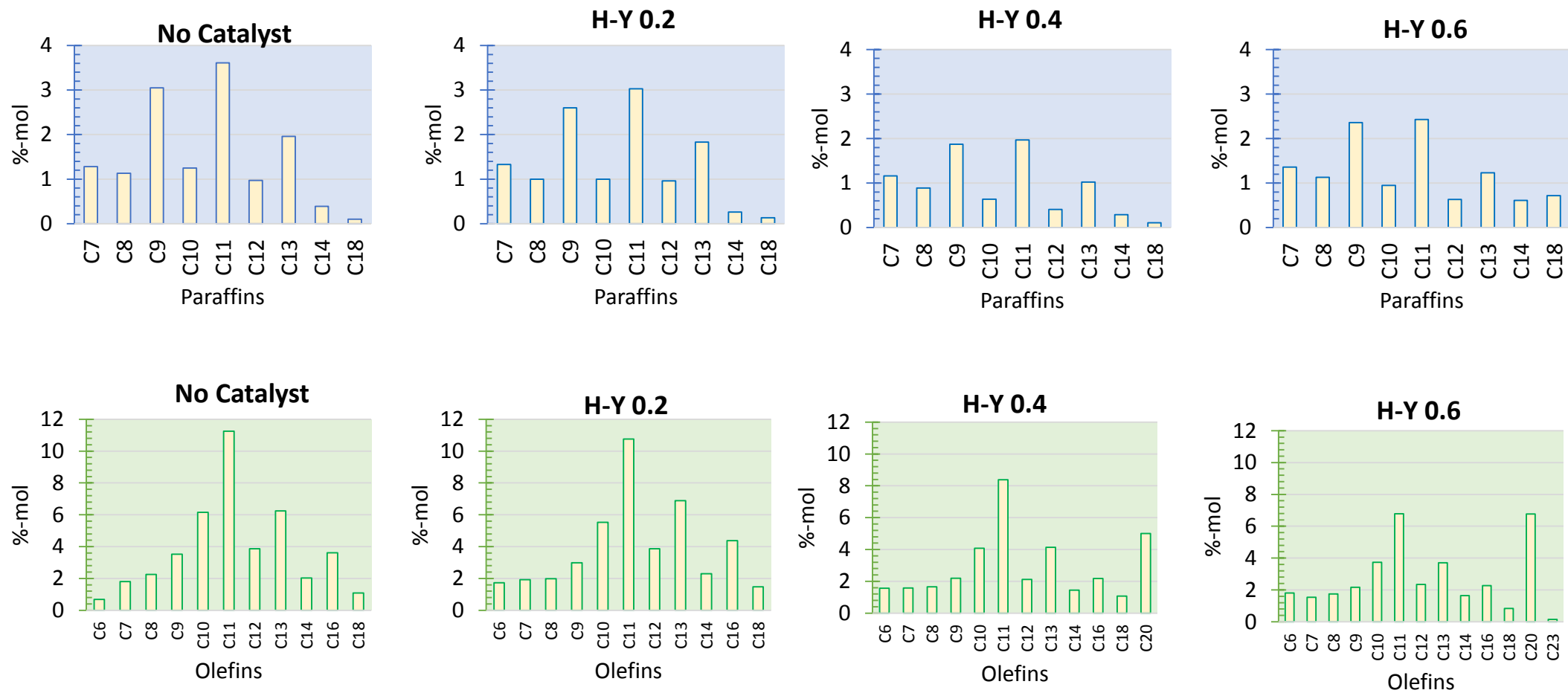
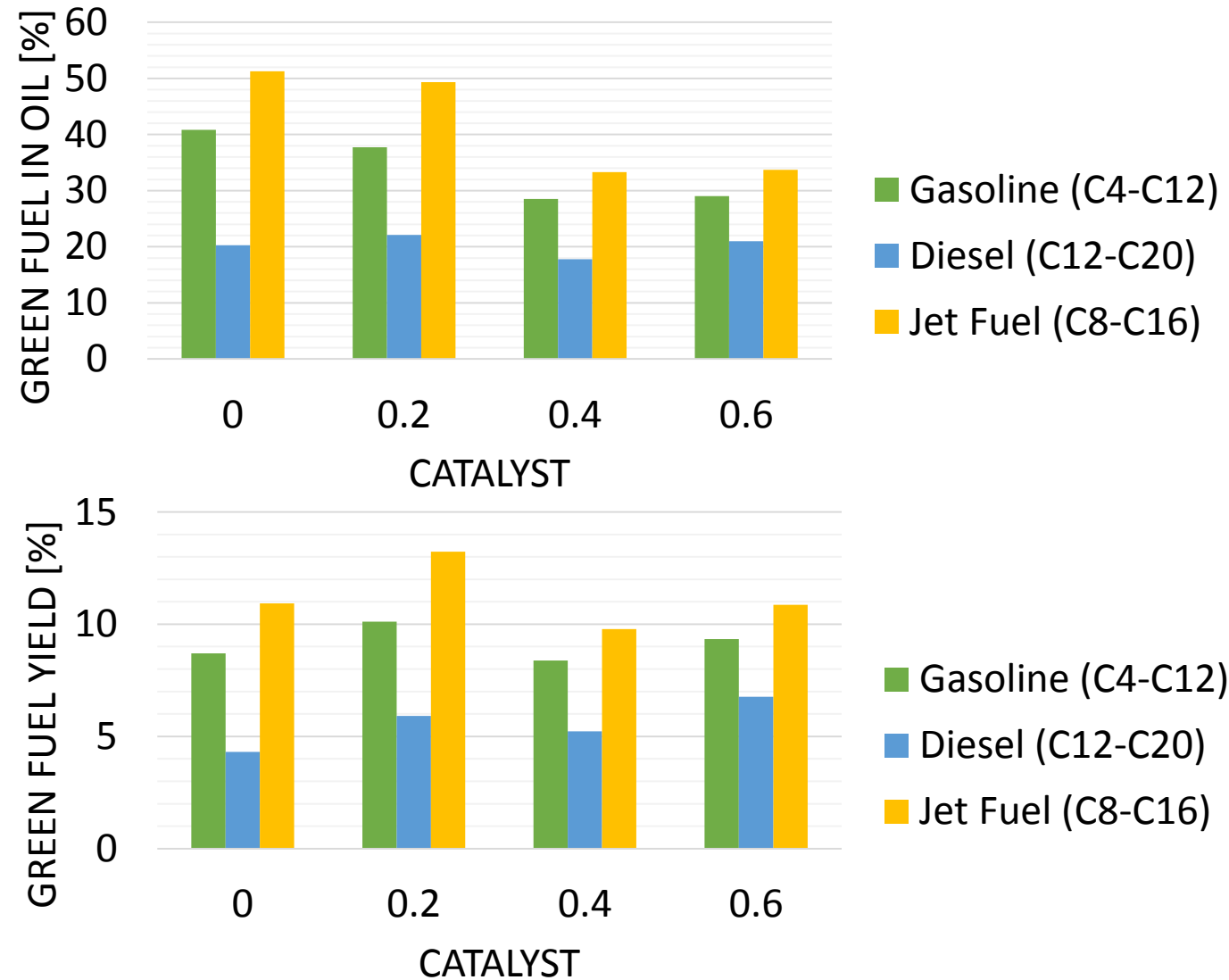


Figure 7. Effect of catalyst zeolite H-Y loading on paraffins and olefins composition.



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

Figure 8. Effect of H-Y loading on green fuel production.

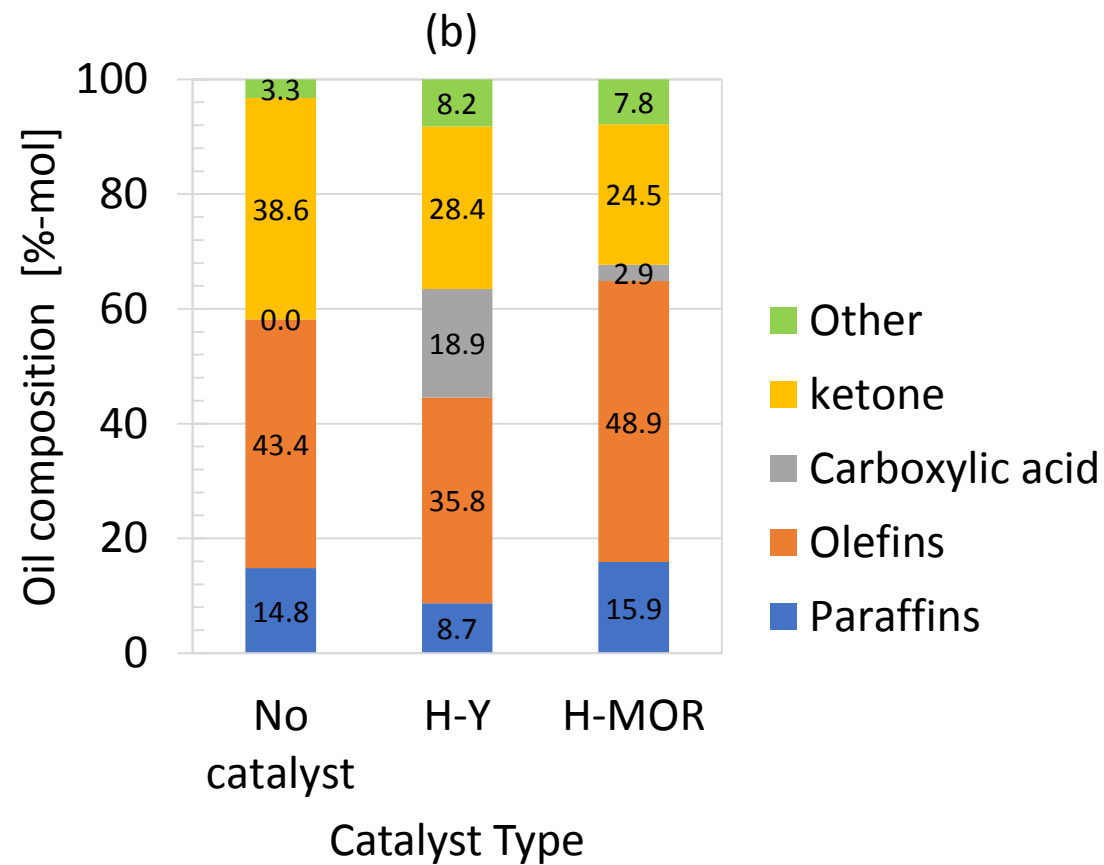
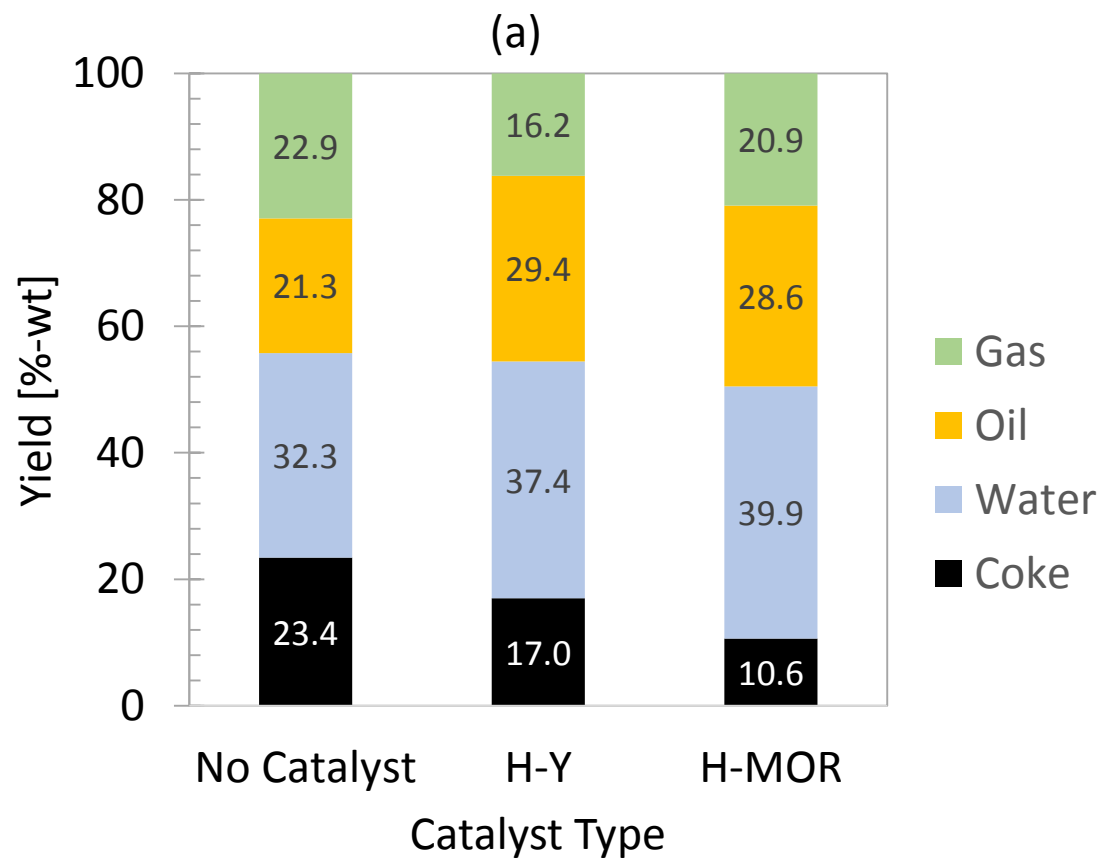


Figure 9. Effect of zeolites type on products yield and oil composition.

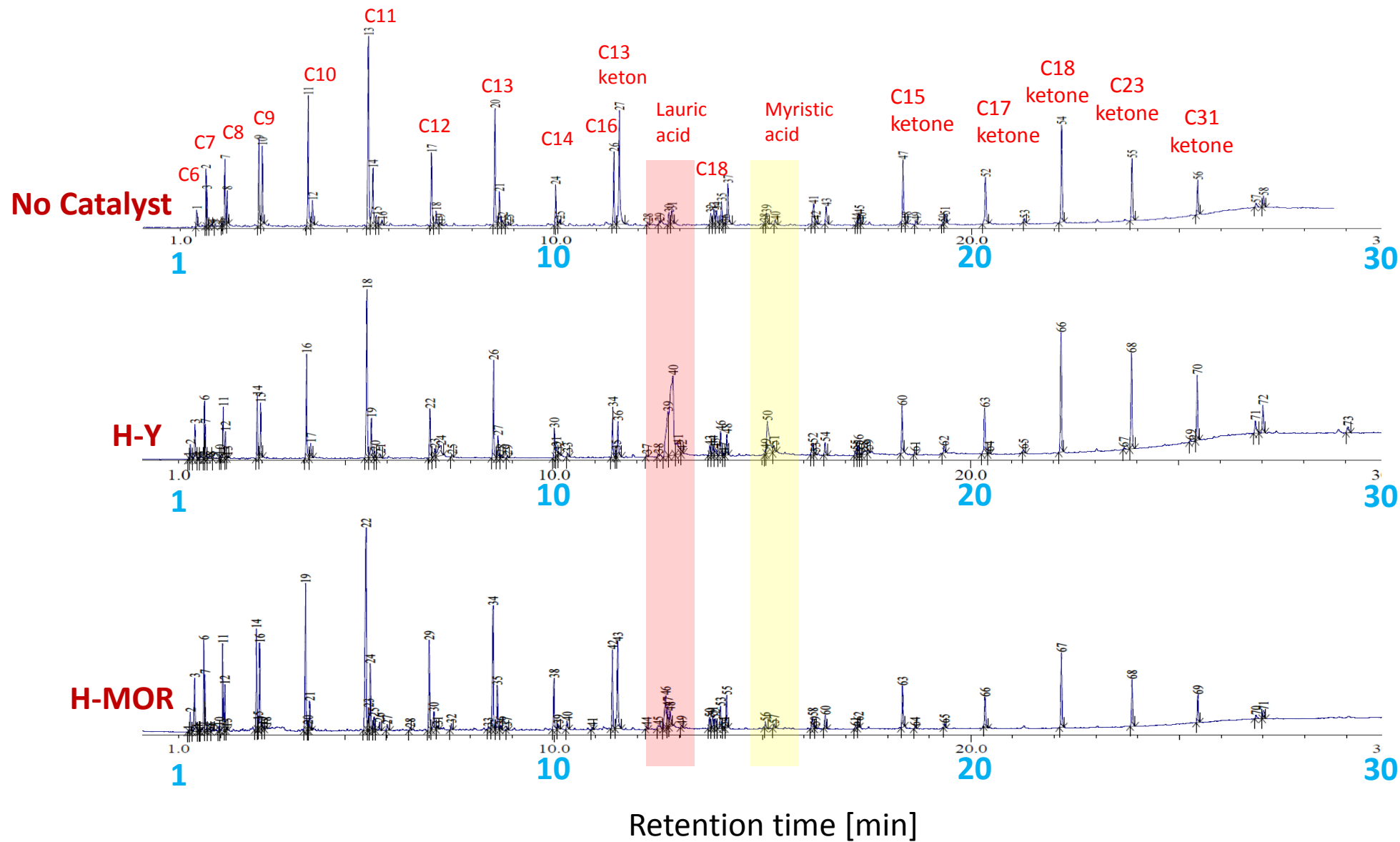


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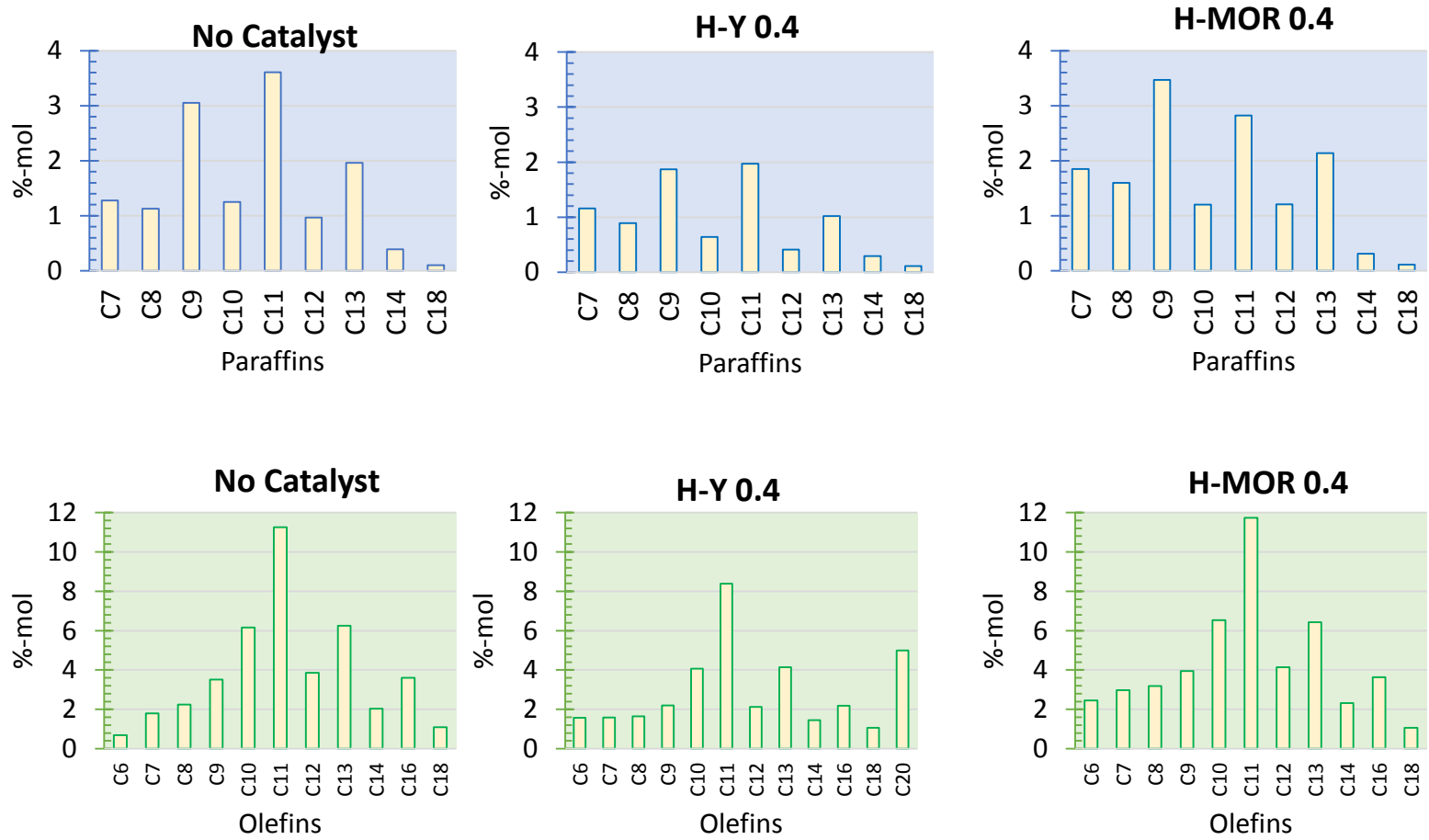
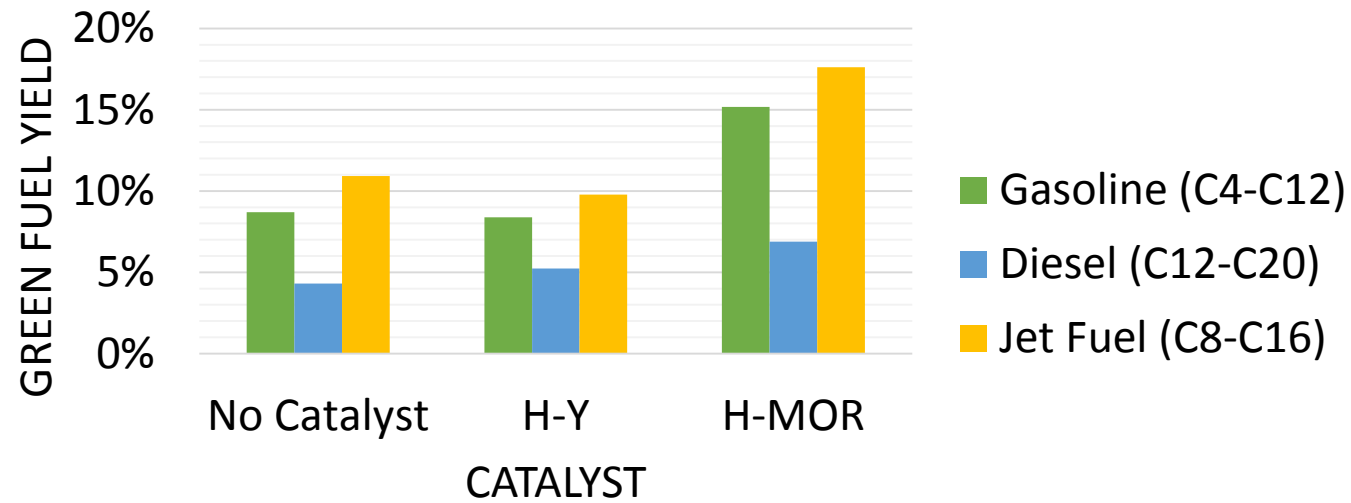
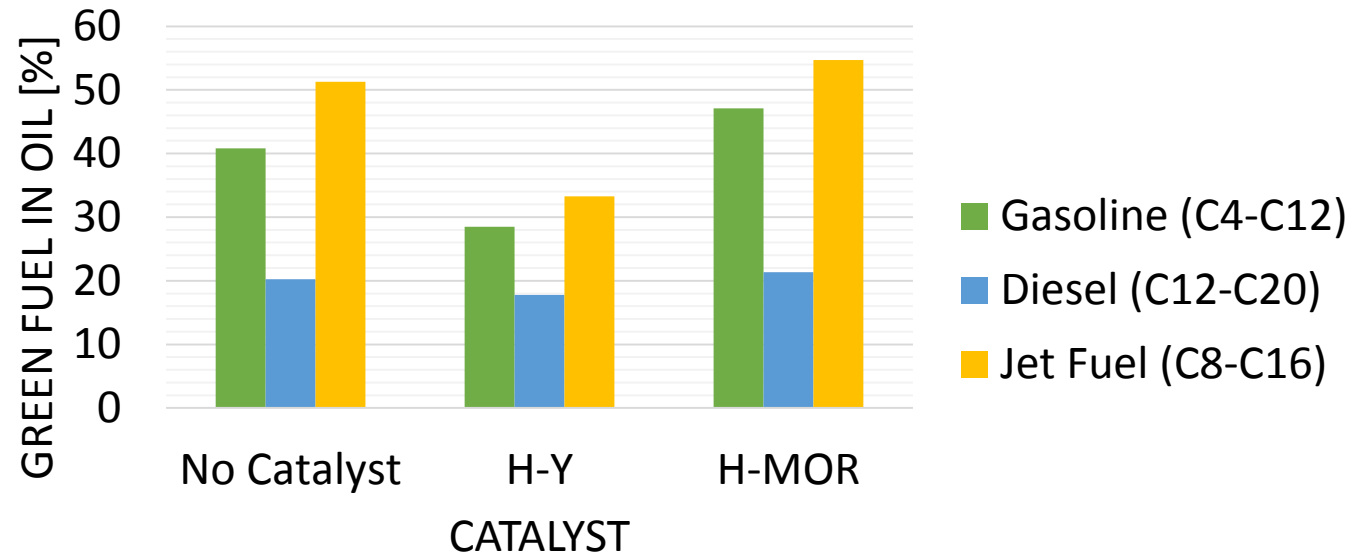


Figure 11. Effect of zeolites type on paraffins and olefins composition.



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

Figure 12. Effect of zeolites type on green fuel production.

Table 2. Characteristic of zeolites sample

Zeolites sample	BET (m²/g)	Si/Al	Framework
Bayah Natural Zeolites	19	4.4	MOR
Zeolite-Y synthetic	650	2.6	FAU

Table 4. Fatty acid content of coconut oil⁶

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

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

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

Table 6. The effect of zeolites type on physical properties of bio oil

Zeolites 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 Sulphur, % mass	0.02
Mercaptan sulphur, %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

Response to Reviewer Comments

Reviewer #1: Catalytic Pyrolysis of Coconut Oil Soap using Zeolites for Bio-hydrocarbon [BCAB-D-21-00404] Production. The manuscript highlights the catalytic pyrolysis of soap in a batch reactor. Below are some points which would help in formatting the manuscript for BCAB:

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Thank you for your advice. We would consider for FTIR analysis in future investigation

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There were several studies study the coke elemental composition and tar. We added literature discussions to improve our manuscript. Please refers to section 3.1 the last paragraph.

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Please refers to section 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.

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12. Check the equation again, reference sources?

Response 12:

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Bio-oil components were analysed by using GC-MS. The percent oxygenate, paraffin, and olefins calculated by % area of each peak appeared in chromatogram divided by total area.

b. Is there no other components such as aromatic, aldehyde, alcohol, etc.?

Response 13b:

Yes, we observed those components in the bio-oil products in small quantities. We revised the manuscript to make clear the impurities components detected. Please refers to Section 3.1 paragraph before Table 3.

14. At 3.5. It is not clear what that means. What is the relationship between the type of catalyst, the amount with the physical properties obtained, explain?

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The bio-oil products physical properties depend on its components. We observed that the bio-oil product resulted from pyrolysis using H-Y contain high carboxylic acids, particularly with sample loading 0.6. The density of carboxylic acid is 0.88 g/mL higher than the paraffinic/olefinic with density average 0.75 g/mL which contributed to make the density of bio-oil from pyrolysis using H-Y high.

15. The conclusion does not include quantitative results which are the optimum conditions and the best results?

The conclusions have not yet culminated in a good conclusion

Response 15:

In this study, we investigated the effect of zeolite loading and the type of zeolites. The optimization part will be conducted in the next works. Thank you for your suggestion.

16. Reference is still lacking, include the results of research in 2021

Response 16:

The manuscript has been revised. We cited recent published articles in 2021.

Reviewer #4: Catalytic Pyrolysis of Coconut Oil Soap using Zeolites for Bio-hydrocarbon Production

BCAB-D-21-00404

Comments:

This manuscript demonstrates the use of zeolite to catalyze pyrolysis of coconut oil soap to produce bio-hydrocarbon, by adjusting the type of zeolite (H-Y and H-M) and the loading of H-Y to improve the quality of bio-oil and reduce the formation of coke. Based on the research results of this manuscript, it seems that H-M is more suitable for producing bio-hydrocarbon and reducing coke yield than H-Y. However, due to the lack of reasonable characterization results, it is difficult to understand the structure-activity relationship of these two catalysts to pyrolysis of coconut oil soap. Experiments have showed that loading 20% of H-Y obtains the highest hydrocarbon yield. Why should the loading of H-M choose 40%? Moreover, the effect of the loading of H-M with better catalytic performance on the pyrolysis properties of coconut oil soap has not been discussed. Therefore, due to the lack of scientific significance and innovation of this manuscript, it is difficult to publish it in Biomass Conversion and Biorefinery with the current quality.

General Response:

The manuscript has been improved. Hopefully, it meets the standard quality to be published in Biomass Conversion and Biorefinery

1. In the abstract section, the authors briefly clarify the purpose, experimental program and main conclusions of this study. However, the method to reduce the formation of coke is vague. Is it through the use of a batch reactor or the addition of a catalyst? In addition, "bio-oil" is a more general writing.

Response 1:

The abstract has been revised. The coke formation was reduced because of using catalyst. The batch reactor was removed from the sentence. We used bio-oil for the whole article.

2. The introduction section is confusing, and it is difficult to find out the significance of the work done in this manuscript for this research field. The second and third paragraphs are used to summarize the influence of different feedstocks, technical routes and operating parameters on pyrolysis plant/animal oil. This has almost nothing to do with this research, but it takes a considerable amount of space to introduce it. Please focus on introducing the current application status of catalysts in the catalytic pyrolysis of oil soaps.

Response 2:

Please refers to paragraph 4-6 to find the current application status of catalysts in the catalytic pyrolysis of oil soaps.

3. "Catalytic pyrolysis over H-Y zeolite reduced the coke formation." is written in part 3.1, please give a more detailed explanation.

Response 3:

The manuscript has been revised. Please refers to part 3.1

4. Figure 5 shows the used catalyst, and simply judged by the color of the solid residue that an increase of the loading can reduce the formation of solid. Although the method of judgment is simple, it seems irrational. The yield of coke is clearly given in Figure 4a, please explain its calculation method. In addition, the article stated that the formation of aromatic hydrocarbons has the same trend as the formation of coke.

Response 4a:

The coke yield was calculated according to equation below

$$\text{coke} = \frac{\text{mass of solid residual} - \text{mass of zeolite}}{\text{mass of soap input}} \times 100\%$$

There are several indications that the coke decreased in the pyrolysis over zeolite.

1. The decreasing of solid residual mass
2. Change of solid colour from black in the thermal pyrolysis to brighten over H-Y 0.6
3. The bio-oil and water yield from pyrolysis using zeolite also increase significantly which suggested that shifting product selectivity from coke to bio-oil

Why are there no aromatic hydrocarbons in the bio-oil components in this study?

Response 4b:

We found aromatic hydrocarbons as trace element. The manuscript has been revised.

5. After adding the catalyst H-Y in part 3.2, the selectivity of hydrocarbons decreased and accompanied by an increase in carboxylic acid products. However, acid products usually cause the pH of bio-oil to decrease, making it corrosive. On the whole, adding H-Y catalyst is not conducive to improving the quality of bio-oil.

Response 5:

Yes, the catalyst H-Y is not recommended because of high carboxylic acid in the bio-oil product. The carboxylic acids products, mainly lauric acid and myristic acid, increased in bio-oil when using zeolite H-Y during pyrolysis (Figure 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 was 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 sodium soap and the protonated zeolite H-Y (equation 2). The more H⁺ provided by zeolites the more carboxylic acids formed.

6. The concepts of coke and char seem to be blurred in this manuscript.

Response 6:

According to Du et.al (2013), char and coke are different depending the mechanisms and in which part the carbon was formed. Char was formed on the wall of pyrolysis reactor and the external surface of catalysts and coke was formed in the micropore of catalysts [1]. However, in our study the char and coke were lumped as coke. The manuscript has been revised. Please refers to introduction section

7. Part 3.3 is difficult to understand. First, please give the NH₃-TPD results of the two catalysts. Secondly, please explain the relationship between the type of acid sites and the formation of coke more rationally. In addition, the two catalysts have different pore sizes and extremely different BET surface areas. What impact will this have on the difference in catalytic performance of the two catalysts?

Response 7:

We did not perform the NH₃-TPD of the catalysts. However, we did in previous work for the MOR catalyst which showed that the strong acid sites observed [2]. The high ratio of Si/Al suggested that the number acid sites of H-MOR were lower than H-Y. Despite the number of acid sites of H-MOR was lower than H-Y, strong acid sites of H-M was probably much higher than H-Y, hence reduce coke production.

8. If the physical properties of jet fuel can be provided for comparison, it may be more helpful to illustrate the effect of zeolite type and loading.

Response 8:

The properties of jet fuel A-1 has been incorporated in the manuscript according to literature [3]. Please refers to Table 7.

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 fractionation distillation to meet commercial Jet A-1 requirement as presented in Figure 1

Some minor issues:

1. Please check the table number carefully. There are two Table 2 in the current manuscript.

Response 1 minor issues:

The manuscript has been revised

2. Please check the format of the reference. For example, page 4, line 56; references 18 and 20.

Response 1 minor issues:

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References

1. 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. <https://doi.org/10.1039/C3GC41581C>

2. Kurniawan T, Muraza O, Hakeem AS, et al (2017) Selective Isomerization of n-Butane over Mordenite Nanoparticles Fabricated by a Sequential Ball Milling-Recrystallization-Dealumination Route. *Energy and Fuels* 31:.. <https://doi.org/10.1021/acs.energyfuels.7b02555>
3. (2000) Handbook of Products. Air BP, Hertfordshire, United Kingdom

Date: 12 Jun 2021
To: "Teguh Kurniawan" teguh@untirta.ac.id
cc: "Achmad Setiawan" achmed.setiawan@gmail.com, "Nurika Andana Putri" nurikaandanaptr@gmail.com, "Anton Irawan" antonirawan1975@gmail.com, "Asep Bayu Dani Nandiyanto" nandiyanto@upi.edu, "Yazid Bindar" ybybyb@fti.itb.ac.id
From: "Martin Kaltschmitt" kaltschmitt@tu-harburg.de
Subject: BCAB: Your manuscript entitled Catalytic Pyrolysis of Coconut Oil Soap using Zeolites for Bio-hydrocarbon Production

Ref.:

Ms. No. BCAB-D-21-00404R1

Catalytic Pyrolysis of Coconut Oil Soap using Zeolites for Bio-hydrocarbon Production

Biomass Conversion and Biorefinery

Dear Dr Kurniawan,

I am pleased to tell you that your work has now been accepted for publication in Biomass Conversion and Biorefinery.

Thank you for submitting your work to this journal.

With kind regards

Martin Kaltschmitt
Editor-in-Chief
Biomass Conversion and Biorefinery

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****Our flexible approach during the COVID-19 pandemic****

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Author's Response To Reviewer Comments

Close

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BCAB-D-21-00404

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The decreasing of solid residual mass

Change of solid colour from black in the thermal pyrolysis to brighten over H-Y 0.6

The bio-oil and water yield from pyrolysis using zeolite also increase significantly which suggested that shifting product selectivity from coke to bio-oil

Why are there no aromatic hydrocarbons in the bio-oil components in this study?

Response 4b:

We found aromatic hydrocarbons as trace element. The manuscript has been revised.

5. After adding the catalyst H-Y in part 3.2, the selectivity of hydrocarbons decreased and accompanied by an increase in carboxylic acid products. However, acid products usually cause the pH of bio-oil to decrease, making it corrosive. On the whole, adding H-Y catalyst is not conducive to improving the quality of bio-oil.

Response 5:

Yes, the catalyst H-Y is not recommended because of high carboxylic acid in the bio-oil product. The carboxylic acids products, mainly lauric acid and myristic acid, increased in bio-oil when using zeolite H-Y during pyrolysis (Figure 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 was 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 sodium soap and the protonated zeolite H-Y (equation 2). The more H⁺ provided by zeolites the more carboxylic acids formed.

6. The concepts of coke and char seem to be blurred in this manuscript.

Response 6:

According to Du et.al (2013), char and coke are different depending the mechanisms and in which part the carbon was formed. Char was formed on the wall of pyrolysis reactor and the external surface of catalysts and coke was formed in the micropore of catalysts [1]. However, in our study the char and coke were lumped as coke. The manuscript has been revised. Please refers to introduction section

7. Part 3.3 is difficult to understand. First, please give the NH₃-TPD results of the two catalysts. Secondly, please explain the relationship between the type of acid sites and the formation of coke more rationally. In addition, the two catalysts have different pore sizes and extremely different BET surface areas. What impact will this have on the difference in catalytic performance of the two catalysts?

Response 7:

We did not perform the NH₃-TPD of the catalysts. However, we did in previous work for the MOR catalyst which showed that the strong acid sites observed [2]. The high ratio of Si/Al suggested that the number acid sites of H-MOR were lower than H-Y. Despite the number of acid sites of H-MOR was lower than H-Y, strong acid sites of H-M was probably much higher than H-Y, hence reduce coke production.

8. If the physical properties of jet fuel can be provided for comparison, it may be more helpful to illustrate the effect of zeolite type and loading.

Response 8:

The properties of jet fuel A-1 has been incorporated in the manuscript according to literature [3]. Please refers to Table 7.

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 fractionation distillation to meet commercial Jet A-1 requirement as presented in Figure 1

Some minor issues:

1. Please check the table number carefully. There are two Table 2 in the current manuscript.

Response 1 minor issues:

The manuscript has been revised

2. Please check the format of the reference. For example, page 4, line 56; references 18 and 20.

Response 1 minor issues:

The manuscript has been revised.

References

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2. Kurniawan T, Muraza O, Hakeem AS, et al (2017) Selective Isomerization of n-Butane over Mordenite Nanoparticles Fabricated by a Sequential Ball Milling-Recrystallization-Dealumination Route. *Energy and Fuels* 31:. <https://doi.org/10.1021/acs.energyfuels.7b02555>
3. (2000) Handbook of Products. Air BP, Hertfordshire, United Kingdom

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