

SYNTHESIS OF ZEOLITE SOCONY MOBIL FROM BLUE SILICA GEL AND RICE HUSK ASH AS CATALYSTS FOR HYDROTHERMAL LIQUEFACTION

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Abstract

Renewable biofuels produced by the hydrothermal liquefaction of rice husks have received much attention because of rapid increases in fuel consumption and corresponding declines in fossil fuel resources. To increase biofuel yields, template-free syntheses of Zeolite Socony Mobil (ZSM) catalysts based on blue silica gel and rice husk ash as silica sources were studied. After ZSM synthesis in a closed reactor at 170°C, the crystallinity and crystalline diameters of the products were determined by X-ray diffraction, affording values of 56.33%–65.81% and 64.3–68.5 nm, respectively. The hydrothermal liquefaction of rice husks with or without a catalyst was conducted in a closed reactor (1200 mm length × 100 mm diameter) at 275°C for 45 min. The light biofuel was separated from the ethanol solvent and heavy biofuel via vacuum evaporation. The ZSM catalysts increased the biofuel yields by 2.9%–6.0%. The light biofuels exhibited heating values, flash points, and viscosities of approximately 4.2–4.3 kcal·g⁻¹, 19°C, and 1.48–1.52 cSt, respectively. However, further studies are required to enhance the activity of the ZSMs and increase the quality of the biofuels.

Keywords: Zeolite Socony Mobil, Hydrothermal liquefaction, Rice husk ash, Blue silica gel, Biofuel.

1. Introduction

Fuels derived from renewable energy sources have received intensive attention because of rapid increases in global energy consumption and the steady depletion of fossil fuel energy sources. The utilization of biomass is an effective strategy for

Nomenclatures

B	Full width at half maximum, FWHM (rad)
D	Crystalline diameter (nm)
k	Constant, 1.14

Greek Symbols

θ	Bragg angle ($^{\circ}$)
λ	Wavelength of X-ray (1.5406 Å)

generating renewable energy because of its abundance as agriculture by-products. Although plentiful, the use of rice husks in the generation of biofuels is not currently appealing due to its low energy density and high ash levels [1].

To increase its utility, biomass such as rice husks can be processed into briquettes [2-4], gaseous fuel by gasification [5-7], and liquid fuel by pyrolysis [8-12]. Unfortunately, briquettes from rice husks still contain significant quantities of ash. Also, gasification and pyrolysis processes are less desirable because of the requisite high temperatures ($\sim 500^{\circ}\text{C}$) [12; 14; 15] and complicated gas purification processes [16; 17]. Furthermore, pyrolysis produces biofuels with viscosities approaching that of biodiesel, ranging from 1.9 to 6 cSt at 40°C [18]. Fuels with high viscosities can cause problems during engine operations, such as increased pumping power requirements and possibility of sedimentation in engines [19]. In addition, biofuels from pyrolysis processes may also have moisture contents up to 25% [10; 20].

In contrast to the aforementioned methods, hydrothermal liquefaction (HTL) offers several advantages. In this flexible process, wet biomass is converted under supercritical conditions into crude biofuels with good efficiency. Benefits of HTL include lower operating temperatures than the other conversion processes, ranging from 250 to 400°C [8; 21; 22]. Also, the HTL process is carried out in a solvent such as water [23] or ethanol [20]. The advantage of using ethanol rather than water as the solvent for the HTL process is its critical temperature (241°C), which is lower than that of water (374°C); thus, the pressure, energy, and time employed for HTL are also significantly reduced when compared with the previous methods.

Catalysts are often used to increase the production of biofuels from the HTL process. These are generally either alkaline catalysts [20], such as KOH, NaOH, LiOH, and CsOH, or acid catalysts. Acidic conditions in the reactor have been found to be best for HTL reactions [24]. One type of promising acid catalyst is the Zeolite Socony Mobil (ZSM). The H-ZSM-5 catalyst has been used to transform ethanol into ethylene under mild conditions [25]. Interestingly, template-free syntheses of ZSMs have been successfully performed by using simple and low cost precursors [26-29], in which the important process parameters were the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio [27; 30], the $\text{Na}_2\text{O}/\text{SiO}_2$ molar ratio [26], and the synthesis temperature [29]. However, no in-depth studies have been performed on the template-free synthesis of ZSMs from cheap and abundance silica sources such as rice husk ash (RHA) and blue silica gel (BSG), for use as catalysts in the HTL of rice husks. Therefore, this study aimed to synthesize ZSMs from rice husk ash and blue silica gel materials, and to study their effects on the HTL processing of rice husks.

2. Experimental Procedures

2.1. Synthesis of ZSMs

Blue silica gel (Sigma Aldrich-S7625), NaAlO_2 (technical, anhydrous, Sigma Aldrich-13404), distilled water (Sigma Aldrich-Z329827), NaOH (97%, Sigma Aldrich-221465), and ethanol (96%, Merck-100967) were used as received. Rice husks were purchased from local farmer in Surakarta, Indonesia. Rice husk ash (RHA) was produced by burning the RHA at a temperature of 900°C . Blue silica gel (BSG) and rice husk ash (RHA) were crushed and then sieved (200 mesh). The compositions of the BSG and RHA were examined by X-ray fluorescence spectroscopy (XRF, PANalytical Minipal 4); results are provided in Table 1.

Table 1. Components in blue silica gel and rice husk ash examined by X-Ray fluorescence.

Sample	SiO_2	P_2O_5	K_2O	CaO	TiO_2	Fe_2O_3
Rice Husk Ash (RHA)	81.70%	2.80%	5.37%	5.95%	0.18%	2.76%
Blue Silica Gel (BSG)	98.10%	-	-	0.44%	0.14%	0.50%

The ZSM synthesis was conducted in a closed stainless steel reactor (250 mm length \times 100 mm diameter) with a maximum pressure of 10 bars. A schematic illustration of the ZSM synthesis reactor is shown in Fig. 1. An electric heater was used to heat the reactor, and the system temperature (pt-100, Tegussa Electronic) was regulated by a thermo controller (Hanyoung Nux). The reactor was also equipped with an electric motor for modulating rotation.

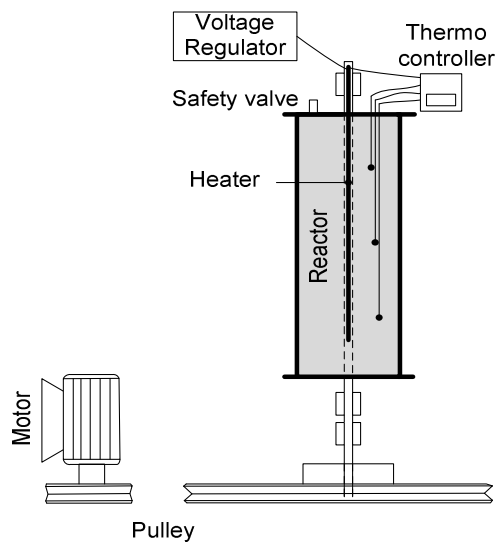


Fig. 1. Scheme of reactor for ZSM synthesis.

The blue silica gel-based ZSM (ZSM-BSG) was synthesized by combining NaOH (6 g) and NaAlO_2 (3.075 g) in H_2O (336 g). The mixture was stirred at 300

rpm using a magnetic stirrer until evenly mixed and the NaOH had dissolved. Then, BSG (45 g) was slowly added with continuous stirring to produce a gel.

The precursor gel was transferred into a closed reactor for the three-stage synthesis of the ZSM [31]. The reactor was rotated at 200 rpm for 5 h without heating, followed by 24 h aging without rotating. In the third stage, the gel was treated hydrothermally in the reactor for 48 h at 170°C and 200 rpm. After the process was completed, the synthesized gel was washed with distilled water and dried in a furnace for 12 h at 80°C.

The rice husk ash-based ZSM (ZSM-RHA) was prepared similarly, using RHA (56.25 g) in place of the BSG.

The ZSMs were characterized by X-ray diffraction (XRD). Sample identification was based on the crystalline peaks measured using monochromatized Cu K α radiation with a wavelength of 0.15046 Å. Diffraction patterns were recorded for 2θ from 5° to 50°. The peak at $2\theta = 22^\circ - 23^\circ$, indicative of ZSM crystal morphology, was selected as the basis for further study. ZSMs based on BSG and RHA were then used as catalysts for HTL.

2.2. Hydrothermal liquefaction of rice husk

The rice husks used in the HTL process were first dried to attain a moisture content of 8% to 12%. Liquefaction was carried out by introducing rice husks (700 g) and 96% ethanol (2100 g) into the reactor and heating to 275°C for 45 min. The HTL process was performed under three sets of conditions: (1) without a catalyst, (2) with ZSM-RHA (35 g), and (3) with ZSM-BSG (35 g). The HTL process of rice husks was conducted in a closed stainless steel reactor (1200 mm length \times 100 mm diameter) which was designed to withstand pressure up to 350 bars. A schematic illustration of the HTL reactor is shown in Fig. 2.

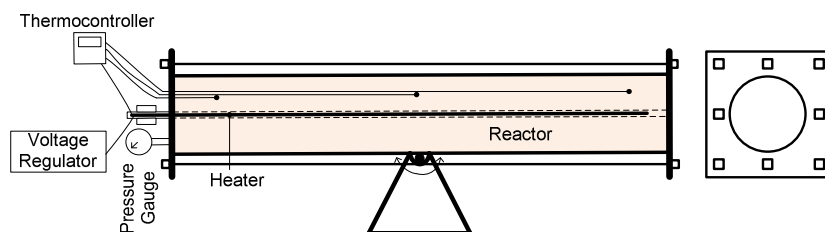


Fig. 2. Scheme of reactor for HTL process.

After HTL completion, the crude biofuels were separated from the ethanol solvent via rotary evaporation performed at 75°C and 55 mmHg. Then, the biofuels were further partitioned into heavy and light fuel fractions via vacuum evaporation at 90°C and 55 mmHg. The physical properties (calorific value, flash point, water content, and viscosity) of the light fuels were determined. The calorific value of the light fuels was measured by bomb calorimeter (IKA C-200) according to the testing standard of ASTM D4809. Measuring the flash point of the light fuels was conducted by the flash point Pensky-Martens closed cup according to ASTM D 93. Meanwhile, Karl Fischer volumetry according to

ASTM D 1744 was used for measuring the moisture content in the light fuels. In addition, the automatic viscosity system according to ASTM D 445 was used for measuring the viscosity of the light fuels.

Furthermore, the compositions of light biofuels were examined by gas chromatography-mass spectroscopy (GC-MS, QP2010S SHIMADZU). The column used was Rastek stabilwakR R-DA with dimension 30.0 m x 0.25 mm. The oven temperature was initially held at 60°C for 5 min, increased to 215°C at 4°C/min, and held for 26.25 min. The injector temperature was 215°C. Carrier gas was helium, and total scan time 70 min. EI mode of ionization was applied and mass scan was from 28 to 600 m/z. For identification of the produced light fuels, library search was carried out using NIST, NBS and Wiley GC-MS library.

3. Results and Discussion

3.1. Characterization of prepared catalysts

Diffraction patterns for the RHA- and BSG-based catalysts are shown in Fig. 3. These were compared against that of a ZSM-5 catalyst (Kansas, USA). The catalysts displayed peaks characteristic of ZSM-5 between 22–23° [28]. XRD analysis revealed that the ZSM-Kansas sample exhibited a ZSM-5 pattern; ZSM-RHA exhibited a ZSM-5(Al) pattern, corresponding to JC-PDF (Joint Committee on Powder Diffraction File) No. 40-0064, or $\text{Na}_{1.54}\text{H}_{3.56}(\text{AlO}_2)_{5.1}(\text{SiO}_2)_{90.9}$; and ZSM-BSG exhibited a ZSM-5 pattern, agreeing with JC-PDF No. 44-0003, or $\text{Al}_2\text{O}_3 \cdot 54\text{SiO}_2$. Thus, the synthesized catalysts were designated as ZSM catalysts, corresponding well with the ZSM-Kansas diffraction data.

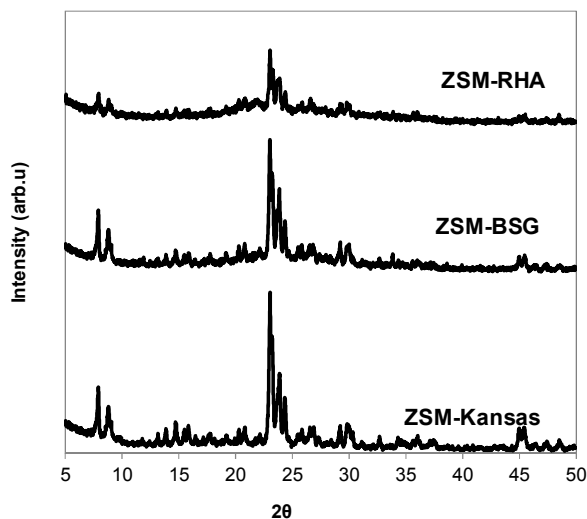


Fig. 3. X-Ray Diffraction patterns.

The crystallinity of the ZSMs was determined by the surface method using the ratio of the crystalline peak area to the total area [32; 33], as shown in Eq. (1). According to Scherrer's equation (Eq. (2)), the crystalline diameter was

calculated from its full width at half maximum (FWHM). The crystallinity and crystalline diameters of the ZSMs are provided in Table 2.

$$\text{Crystallinity} = \frac{\text{Total area} - \text{Crystalline peak area}}{\text{Total area}} \quad (1)$$

$$D = \frac{k\lambda}{B \cos\theta} \quad (2)$$

The crystallinity of ZSM-BSG was superior to that of ZSM-RHA because a number of oxides found in RHA, particularly those based on alkali metals, may inhibit the crystallization process. Alkali metals in RHA can accelerate the transformation of amorphous SiO₂ into cristobalite or tridymite by lowering the transition temperature [34]. The declining transition temperature of SiO₂ induces a larger difference in the transition temperature between SiO₂ and Al₂O₃, inhibiting the doping of Al atoms into the SiO₂ lattice. The lower crystallinity of ZSM-RHA may have resulted from alkaline compounds that inhibited nucleation, so that at a fixed temperature and time, ZSM-RHA crystals did not grow as well.

The crystalline diameter of ZSM-RHA also differed slightly from those of ZSM-BSG and ZSM-Kansas, as shown in Table 2. The ZSM synthesized from RHA has a larger amount of Na⁺ than BSG. Na⁺ plays a role in controlling the basicity of the catalyst, whereas Al³⁺ controls the acidity. Na⁺ may also improve nucleation [27], leading to a slight increase in the crystalline diameter. The nano-sized of crystalline diameters of ZSM-RHA and ZSM-BSG may lead to a better exchange of ions during the hydrothermal liquefaction reaction.

Table 2. Crystallinity and crystalline diameters of ZSMs.

Catalyst	2θ	B (FWHM)	D (nm)	Crystallinity
ZSM-Kansas	23.10	0.175	56.0	47.94%
ZSM-BSG	23.02	0.155	64.3	65.81%
ZSM-RHA	23.03	0.150	68.5	56.33%

3.1. Effects of synthesized catalysts on biofuel production from HTL

The ZSM-RHA and ZSM-BSG catalysts were used in the hydrothermal liquefaction of rice husks, and the results were compared against biofuels produced by the corresponding transformation without a ZSM catalyst. The biofuel yields from the HTL processes were calculated using Eq. (3); the product compositions as determined by GC-MS are depicted in Table 3.

Table 3. Product compositions from HTL processes.

Treatment in HTL	Gas	Solid	Light Fuel	Heavy Fuel
Without Catalyst	18.47%	39.90%	19.86%	21.77%
ZSM-BSG	12.86%	44.29%	21.14%	21.71%
ZSM-RHA	13.00%	42.86%	23.57%	20.57%

The biofuel yield produced using the ZSM-RHA catalyst was higher than that of ZSM-BSG because of the greater amount of aluminium found in the ZSM-RHA. The aluminium quantities in the ZSMs are evident from the molecular formulas of the two catalysts. The aluminium in ZSM plays a significant role in

increasing the acidity of the catalyst. A more acidic catalyst facilitates the dehydration reactions that lead to higher yields of biofuels.

$$\text{Biofuel production} = \frac{\text{mass of biofuel}}{\text{mass of biomass}} \times 100\% \quad (3)$$

Table 3 reveals that the biofuel quantities (heavy and light fuels) produced from the HTL process using the ZSM catalysts were greater than that from the process without a catalyst. ZSM-RHA and -BSG increased the biofuel yields 6.0% and 2.9%, respectively. The results agreed with a previous study in which the addition of an acid catalyst (pH = 3) by addition of chloride acid improved the biofuel yield by 4.3% [24]. In that previous study, the HTL process was conducted at 300°C with a residence time of 30 min. Our results reveal that the addition of a ZSM can increase the yield of biofuels produced by the HTL process.

The conversion of biomass by HTL process follows three sequential steps: dehydration reaction, decarbonylation, and cracking as shown in Fig. 4. The main compounds produced from HTL process of RH without catalyst are propanoic acid, butanoic acid, acetic acid, propane, furfural, and butanol where the scheme is shown in Fig. 5.

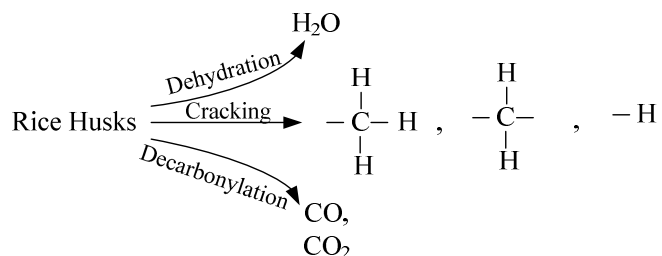


Fig. 4. Three Sequential Steps in HTL Process: Dehydration, Decarbonylation, and Cracking Reaction.

Furthermore, the function of the ZSM catalysts is to boost the reaction rate. Compounds with high activity were cracked firstly, which generated gaseous hydrocarbons and micro-cokes. This phenomenon is evidenced by the increasing content of solids produced from the HTL process using ZSM catalysts. The active compounds produced via cracking reaction such as; -OH, -H or -CH₂ were adsorbed on the surface of ZSM catalysts [35]. When other active compounds were adsorbed to the catalyst surface, the carbon chain became longer to form -CH₃ or -CH₂CH₂CH₂CH₂- compounds. Some of the -CH₂CH₂CH₂CH₂- compounds desorbed from the surface of the ZSM catalysts and attacked with -H groups to form propane (C₄H₈).

In addition, micro-cokes produced by the HTL process might clog and deactivate the ZSM catalysts. The cracking of the less reactive compounds, like propanoic acid or acetic acid, was interrupted. Thus, the concentration of the butanoic acid compounds in the light fuels produced by the HTL process with the ZSM catalysts increased significantly.

Meanwhile, the pathways of HTL process with ZSM-RHA catalysts are relatively different with that of ZSM-BSG catalysts. In the ZSM-RHA catalysts, the glucose might be cracked directly into acetic acid compounds leading to the increase of acetic acid in the light biofuels. Another possible pathway for increasing the acetic acid by ZSM-RHA catalysts was that at a temperature of 200°C, the ethanol solvent might oxidize into acetic acid via $\text{CH}_3\text{CH}_2\text{OH} + \text{CO}_2 \rightarrow \text{CH}_3\text{COOH} + \text{HCOH}$ [20]. However, the more appropriate reaction mechanisms needed to be further investigated.

In addition, the dehydration reaction involved in the HTL process was started with the release of OH^- ions from the catalyst and bound with H^+ ions to form H_2O . The dehydration reaction is responsible for the increased moisture content in the biofuel products. Regardless, the increase yield of moisture was higher than that of dry light fuels. It is very possible because ZSM catalysts increased also the reaction rate of hydrolysis reaction and each hydrolysis process always produced compounds and H_2O in light fuels. As depicted in Table 5, biofuels produced by HTL process with the ZSM-BSG and ZSM-RHA catalysts had higher moisture contents than that produced via the HTL process without catalysts.

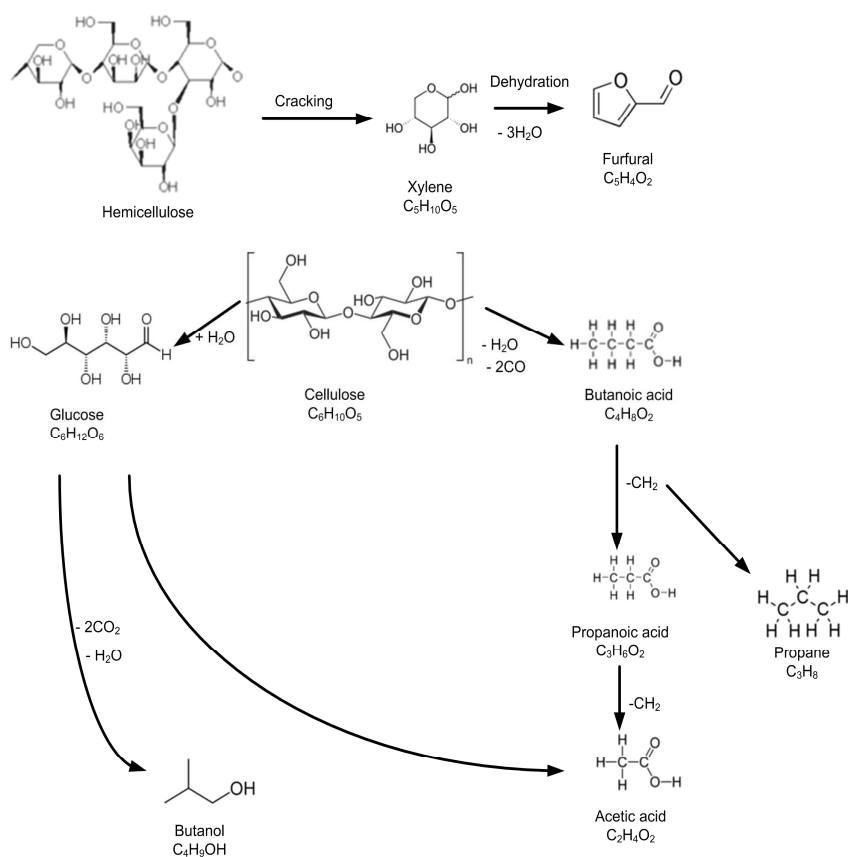


Fig. 5. Scheme of the Mechanisms of HTL process to produce the main compounds of light fuels.

Meanwhile, the decarbonylation reaction is the carbon break up reaction while releasing CO or CO₂. The decarbonylation reaction took place faster because of the peroxide compounds (e.g. Al₂O₃) on the surface of the ZSM catalyst that helped to break up the active core of acids and the C-C bonds. Therefore, because of the decarbonylation reaction or carbon-bond splitting reaction, a small amount of short-chain hydrocarbons was also detected in the resultant biofuels by GC-MS (Table 4).

Table 4. Compounds in biofuels detected by GC-MS.

Compounds	HTL	HTL	HTL
	without Catalyst	with ZSM-BSG	with ZSM-RHA
Propanoic acid	28.70	9.32	21.75
Butanoic acid	13.17	31.26	24.40
Acetic acid	11.21	0.00	9.04
Propane	10.02	7.42	11.69
Furfuryl formate	6.85	0.00	0.00
Butanol	4.68	0.00	0.00
Cyclopentane	3.41	4.43	6.08
Pyrrrole	3.15	0.61	3.04
Pentanol	2.67	1.88	1.11
Furan methanol	2.65	3.79	2.49
Propanol	2.60	0.75	2.90
Phenol	1.79	3.42	3.10
Butanone	1.72	1.72	0.00
Acetone	1.67	0.00	2.27
Butanedioic acid	1.34	2.65	1.16
Dioxalane	1.29	0.00	3.00
Pentanoic acid	1.15	5.23	0.91
Butane	1.12	0.64	0.00
Pentanone	0.81	0.69	0.00
Butyl-furan	0.00	17.67	5.59
Hexanoic acid	0.00	0.00	0.57
Diethyl succinate	0.00	1.05	0.61
Benzenedicarboxylic acid	0.00	0.08	0.28
Butadienol	0.00	0.65	0.00
Cyclopentanone	0.00	0.90	0.00
Pentane	0.00	1.22	0.00
Butadiene	0.00	0.71	0.00
Furancarboxylic acid	0.00	1.70	0.00
Cyclohexanone	0.00	0.08	0.00
Methoxybenzene	0.00	0.43	0.00
Pyrimidine	0.00	0.75	0.00
Benzene	0.00	0.20	0.00
Bicycle	0.00	0.40	0.00
Tetraxyloxane	0.00	0.33	0.00

The physical properties of the biofuels are shown in Table 5. The viscosities of the three biofuels were similar (~1.50 cSt), and resembled the viscosity of biodiesel according to the ASTM D6751 standard (i.e. 1.9–6.0 cSt) [19]. Moreover, biofuels produced from the HTL process without catalysts had higher heating values than those from the HTL process employing ZSM-BSG and ZSM-RHA catalysts. The

main reason for the decline in the heating values of biofuels obtained from the HTL processes with ZSMs is the increase in the moisture content resulting from the dehydration reaction. The increased moisture content also raised the flash point, which was similarly sensitive to the compounds comprising the biofuels. The products from the HTL processes with ZSMs contained a higher content of butanoic acid, which has a higher flash point (72°C) than propanoic acid (54°C). However, the flash point of the biofuels produced by the HTL process was still lower than the flash points of biodiesels such as soybean oil (69°C), cotton seed oil (70°C), rape seed oil (170°C), and rubber seed oil (130°C) [36].

Table 5. Properties of Biofuels from HTL Process.

Treatment in HTL	Viscosity (cSt)	Flash Point (°C)	Heating Value (cal/g)	Moisture Content (%)
Without Catalyst	1.51	15	4956	14.58
ZSM-BSG	1.48	19	4291	18.52
ZSM-RHA	1.52	19	4247	22.16

4. Conclusions

Template-free ZSM catalysts were successfully synthesized from both blue silica gel and rice husk ash. The produced ZSMs were subsequently used as catalysts for the hydrothermal liquefaction of rice husks to produce biofuels. The crystallinity and the crystalline diameters of the prepared catalysts were in good agreement with a ZSM-Kansas standard, having values of 65.81% and 64.3 nm for ZSM-BSG and 56.33% and 68.5 nm for ZSM-RHA, respectively. ZSM-RHA and ZSM-BSG increased the biofuel yields from the HTL of rice husk by 6.0% and 2.9%, respectively. The biofuels produced by the HTL of rice husks with ZSM catalysts had heating values, flash points, and viscosities of approximately 4.2–4.3 kcal·g⁻¹, 19°C, and 1.48–1.52 cSt, respectively. In future studies, it would be interesting (1) to enhance ZSM quality by purifying the silica from RHA; (2) to increase the quality of biofuels by employing the HTL process for coal or for a biomass with higher carbon content such as wood; and (3) to utilize the biofuels produced from the HTL process as alternative liquid fuels.

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