

Hydrotreating of Jatropha Oil over Alumina Based Catalysts

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ABSTRACT: Hydrotreatment of nonedible jatropha oils over PtPd/Al₂O₃ catalyst and NiMoP/Al₂O₃ catalysts was investigated under conditions of 330–390 °C, 3 MPa and 2 h⁻¹ in a fixed-bed reactor. A significantly high yield range of about 82 wt % of liquid hydrocarbon products was achieved over all catalysts. Moreover, the liquid hydrocarbon products have low acid number, suitable density and viscosity, and quite high cetane index. The oil can be a high-performance additive for diesel oil. The oxygen removal pathway of jatropha oil over PtPd/Al₂O₃ catalyst is primarily compiled through decarboxylation and/or decarbonylation, but over NiMoP/Al₂O₃ catalysts, the oxygen removal pathways are executed primarily by hydro-deoxygenation. A long-term experiment was conducted over catalyst A (NiMoP/Al₂O₃). Results show that catalyst A starts deactivation from reaction time of 120 h. The sulfide catalyst conversion to oxide catalyst is regarded as the main reason for deactivation. The deactivated catalyst can be reused after regeneration treatment.

1. INTRODUCTION

With the declining availability of petroleum resources, deterioration of the world environment, and the increased demand for fuels by emerging economies, it is imperative to develop new routes to produce green renewable fuels to substitute conventional fossil-derived ones. Using renewable biomass resources to produce biofuels is regarded as an attractive alternative. Biofuels present many benefits including domestic production, less greenhouse gas emissions, less dependence on fossil fuels, improvement of rural economies, and increased national energy security.¹ Consequently, a great interest has developed in the exploration of efficient processes for producing new-generation biofuels from biomass resources. Among these, using jatropha oil, a nonedible vegetable oil, to produce biofuels is a promising route for many reasons: high energy density, easy conversion to liquid biofuel, high oil production at a low price, ease of establishing and maintain jatropha plantations, government support, etc.²

In all vegetable oils, the main constituent is triglycerides. The high viscosity and instability deriving from triglycerides are the most challenging obstacles to the use of vegetable oil directly as a diesel fuel. Several processes have been developed to resolve that problem in recent years, such as transesterification, pyrolysis, blending with petrodiesel, microemulsification with alcohols, and hydrotreatment.³ Hydrotreatment processing has attracted great attention and is now regarded as among the best options for refiners, agricultural producers, and forest product producers because of its superior product properties, lower capital investment for production, and lower environmental impact, especially in view of the benefits to refiners, agricultural producers, and forest product producers.⁴

First, co-hydrotreating of vegetable oils with petroleum derived fractions using existing hydrotreating infrastructure in refineries has attracted much attention.^{1,5} However, because of the bad cold flow properties of the hydrotreated products, the added proportion of vegetable oil should be strictly limited. Then, hydrotreating of vegetable oils such as palm oil,⁶ rapeseed oil,^{7–10} sunflower oil,¹¹ jatropha oil,¹² and fatty acid

esters^{13,14} over traditional hydrodesulfurization catalysts such as sulfided NiMo/Al₂O₃, CoMo/Al₂O₃, and NiW/Al₂O₃ have been investigated by some researchers. Results show that complete conversion of triglycerides can be achieved in suitable conditions, but detailed information about catalyst lifetime, physicochemical properties of liquid hydrocarbon products, and deactivation and regeneration problems of catalysts were not presented. Hydrotreatment of sunflower oil over oxide CoMo/Al₂O₃ and NiMo/Al₂O₃ was reported by Krár and co-workers.¹⁵ Although this process is free of sulfur, it is noteworthy that the problem of high reaction temperature and low deoxygenation ability of the oxide catalysts must be solved. Although the liquid hydrocarbon products of these processes have a high cetane number (70–100), they mainly consist of *n*-paraffin. Their cold flow properties are so unfavorable that their application as diesel fuels is strictly limited. To resolve the cold flow properties problems, isomerization of *n*-paraffins to their branched isomers, which have been widely applied in petroleum industries such as dewaxing of lubricating oil, is regarded as an extremely feasible method. Hydroisomerization of *n*-paraffins produced from hydrodeoxygenation of vegetable oil over some developed isomerization catalyst such as Pt/ZSM-22 and Pt/SAPO-11 in a separate reactor was reported.^{16,17} High-quality products are obtainable after the two processes, but the costs brought by the two-step process should be noted.

Although many papers about hydrotreatment of vegetable oil and model compounds were reported, few papers describe work in properties of liquid hydrocarbon products and catalyst lifetime in the view of industry production. Moreover, efficient reduced catalysts are more desirable than sulfide catalysts due to environmental factors, but there are also few papers reported that are efficient hydrodeoxygenation (HDO) of vegetable oil feasible over reduced catalysts. Thus, in this paper, hydrotreat-

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ment of jatropha oil over two sulfided NiMoP/Al₂O₃ catalysts and one reduced PtPd/Al₂O₃ catalyst under suitable reaction conditions was conducted. Then, their catalytic performances were compared. Moreover, physicochemical properties of the liquid hydrocarbon products, effects of metal on the deoxygenation pathway, long-term experiments, deactivation, and regeneration of the NiMoP/Al₂O₃ catalyst were studied further.

2. EXPERIMENTAL SECTION

2.1. Feedstocks and Catalysts. The feedstock used for catalyst activity evaluation was a kind of crude jatropha oil supplied by CREATA-IPB and produced in Bogor, Indonesia. Some physical and

Table 1. Main Properties of Jatropha Oil

	density (g/cm ³)	dynamic viscosity (mPa·s/ 25 °C)	acid value (mg KOH/g)	gum content (mg/g)	free fatty acid content (wt %)
jatropha oil	0.91	21.17	8.48	8.7	4.47

chemical properties of crude jatropha oil are presented in Table 1. Density and Dynamic viscosity were determined using a Hydrometer (JIS-II) and a Dynamic Viscometer (SV-10A; Vibro). According to the ASTM-D974, the acid number was determined by titration using a standard solution of potassium hydroxide in ethanol. The gum content was determined based on ASTM-D381.

All catalysts were prepared using conventional successive impregnation method according to the reported procedure.¹⁸ A commercial γ -Al₂O₃ (surface area, 273 m²/g; pore volume, 0.771 cm³/g) supplied by Nippon Ketjen Co., Ltd. was crushed and screened to provide 20-mesh to 80-mesh and used as the support for the following impregnation. PtPd/Al₂O₃ catalyst containing 2 wt % Pt and 10 wt % Pd was prepared using aqueous solutions of H₂PtCl₆ and PdCl₂, in which Pd was introduced first. The other two catalysts, A and B (NiMo/Al₂O₃), were prepared using aqueous solutions of (NH₄)₂HPO₄, Ni(NO₃)₂, and (NH₃)₆Mo₇O₂₄, successively. After impregnation, the samples were dried at 105 °C for 2 h in air and then calcined at 450 °C for 10 h in air.

2.2. Catalyst Characterization. Elemental analysis was conducted using an X-ray fluorescence instrument (EDX-800; Shimadzu Corp.). The samples were pressed into disks before analysis. Specific surface areas and pore sizes were determined from the nitrogen adsorption and desorption isotherms and recorded at -196 °C using a Belsorp-mini II device. Before the measurements, the samples were degassed under vacuum at 400 °C for 1 h. The specific surface areas and pore volumes were calculated using the BET (Brunauer–Emmett–Teller) method. Then, the average pore sizes were calculated from desorption isotherm branches using the Barrett–Joyner–Halenda method.

2.3. Catalyst Activity Measurements. Details of the apparatus were also described in an earlier report.¹⁹ In short, the reactions were conducted with a fixed-bed flow microreactor (ϕ 8 mm i.d.). About 3 mL of catalyst was loaded and sandwiched by quartz sands in the reactor. The feedstock was injected by a high-pressure pump into the hydrogen stream. The reaction was conducted at 330–390 °C, 3 MPa of total pressure, LHSV (liquid hourly space velocity) = 2 h⁻¹, H₂/feed ratio = 600 (v/v). Before reaction, the NiMoP/Al₂O₃ catalysts were sulfided in situ at 400 °C and atmospheric pressure by a mixture of 5 vol % H₂S and 95 vol % H₂ at a rate of 50 mL/min for 3 h, and the PtPd/Al₂O₃ catalyst was reduced in situ at 400 °C and atmosphere pressure by a H₂ flow at a rate of 50 mL/min for 3 h. Reaction products were separated into gas and liquid first; then, the liquid products were separated into water and oil phases.

Two gas chromatographs (17A and 14B; Shimadzu Corp.), each equipped with a FID (flame ionization detector) and a commercially available column (DB-1, 0.25 mm \times 60 m), were used to analyze the

hydrocarbons in the gaseous products and liquid products, and a gas chromatograph mass spectrometer (GCMS-QP5050A; Shimadzu Corp.) equipped with the same capillary column (DB-1, 0.25 mm \times 60 m) was used to identify the components of the reaction hydrocarbon products. Another gas chromatograph with a TCD (thermal conductivity detector) and a commercial column (Unibeads C, 3 mm \times 3 m) was used to determine other components, such as CO and CO₂, in gaseous products. In addition, simulated distillation of the liquid hydrocarbon products were carried out using a Shimadzu 2025 gas chromatograph according to the ASTM-2887 procedure.

3. RESULTS AND DISCUSSION

3.1. Feedstock and Catalysts. Similarly to other vegetable oils, triglycerides are the main components of jatropha oil. They can be hydrolyzed to three fatty acid molecules and a glycerol molecule. However, jatropha oil also contains a small amount of free fatty acid. From Table 1, results show that the feedstock has an acid value of 8.48 mg KOH/g, which results from the high free fatty acid contents. Fatty acid compositions of the feedstock were determined using gas chromatography after transesterification and esterification with methanol. The fatty acid composition of jatropha oil and their contents are presented in Table 2. From the analysis results, fatty acids

Table 2. Fatty Acid Composition of Jatropha Oil (C %)

fatty acid	structure	formula	composition
palmitic acid	C16:0	C ₁₆ H ₃₂ O ₂	15.56
linoleic acid	C18:2	C ₁₈ H ₃₂ O ₂	34.06
oleic acid	C18:1	C ₁₈ H ₃₄ O ₂	42.86
stearic acid	C18:0	C ₁₈ H ₃₆ O ₂	7.29
gadoleic acid	C20:1	C ₂₀ H ₃₆ O ₂	0.23

mainly found in jatropha oil are linoleic, oleic, palmitic, stearic, and gadoleic acid, each of which has a straight chain structure. The fatty acids with a carbon number of 16 and 18 have carbon molar percentages of 15.56% and 84.21%, respectively. The saturated and unsaturated fatty acid contents are respectively 22.85% and 77.15%.

The metal loading of the three catalysts is presented in Table 3. The theoretical loadings of Pt and Pd in PtPd/Al₂O₃ catalyst were respectively 2 wt % and 10 wt %. For catalyst A and catalyst B, they have the same kinds of loading metal. Their respective loadings of Ni, Mo, and P are 3.1 wt %, 15.9 wt %, 5.8 wt %, and 3.0 wt %, 10.8 wt %, 2.6 wt %. The textural properties derived from nitrogen adsorption–desorption isotherms of the entire calcined catalysts are also shown in Table 3. The specific surface areas of all catalysts are 193–228 m²/g. Due to the relatively high loading amount, catalyst A and catalyst B have lower specific surface areas than that of the PtPd/Al₂O₃ catalyst, which also resulted in the smaller average pore diameter and lower total pore volume.

3.2. Analysis of Products in HDO of Jatropha Oil. The compositions of products were similar for all HDO reactions on three catalysts. The gaseous products consisted of large amounts of propane and small amounts of other light hydrocarbons of C₁ to C₅. Small amounts of carbon dioxide and carbon monoxide were detected using a TCD, as well. Liquid products had two clear and colorless phases of oil phase and water phase for reaction temperatures higher than 330 °C, whereas the liquid products became cloudy and contained a suspension of white crystals when the reaction temperature was lower than 330 °C (when the catalysts were inactive, the liquid products became cloudy and contained a suspension of white

Table 3. Chemical Analysis and Textural Properties of Catalysts

catalyst	chemical composition, wt%					textural parameter		
	P	Ni	Mo	Pt	Pd	S_{BET} (m ² /g)	V_{total} (cm ³ /g)	d_{avg} (nm)
PtPd/Al ₂ O ₃	—	—	—	2	10	228	0.632	11.1
catalyst A	2.6	3.1	15.9	—	—	195	0.608	10.3
catalyst B	5.8	3.0	10.8	—	—	193	0.601	10.4

crystals). The oil phase, which was regarded as liquid hydrocarbon products, was separated and determined using the GC-MS technique. The composition distribution of the liquid hydrocarbon products was analyzed using GC-FID. Figure 1 portrays a typical chromatogram of liquid hydrocarbon

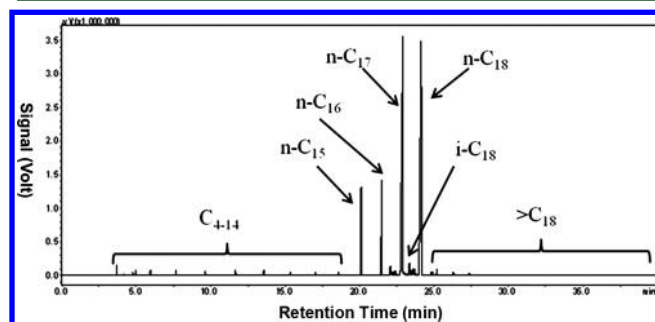


Figure 1. Typical chromatogram of the liquid hydrocarbon product.

products. The results of analysis show that the liquid hydrocarbon products represent a simple mixture containing mainly *n*-paraffins of C_{15–18}. Aside from *n*-paraffins of C_{15–18}, the liquid hydrocarbon products also contain small amounts of alkanes of C_{4–14} and iso-paraffins of C_{15–18}, with trace amounts of cycloalkanes and aromatics of C_{15–18}. Some oxygenates (e.g., fatty acid, fatty alcohol, monoglycerides, diglycerides) were found in some cases; the contents of the oxygenates were very low (<0.05%). These oxygenates are contained in C₁₈₊.

3.3. Catalytic Activity of Different Catalysts. Deoxygenation of vegetable oil is thought to proceed along three pathways, decarboxylation, decarbonylation, and hydrodeoxygenation, by which the oxygen content of triglyceride is converted, respectively, to CO₂, CO, and water.^{1,10} These byproducts and other lighter hydrocarbons (mainly propane), which derive from the hydrogenation of glycerin and cracking, bring about a mass loss of the yield of the liquid hydrocarbon products. The theoretical value of the yield of liquid hydrocarbon products can be estimated if the cracking products are ignored. Therefore, the available theoretical yield of liquid hydrocarbon products can vary from 81.1 wt % (deoxygenation only by decarboxylation or decarbonylation) to 86.0 wt % (deoxygenation solely by hydrodeoxygenation).

Hydrogenation of jatropha oil over three different catalysts was conducted in conditions of $T = 350$ °C, $\text{LHSV} = 2$ h⁻¹, $P = 3$ MPa, $\text{H}_2/\text{oil} = 600$ mL/mL. Table 4 presents product yields and components of liquid hydrocarbon products obtained over different catalysts after 5 h of reaction time. A significantly higher yield (81.2–83.9 wt %) of liquid hydrocarbon products was achieved for all catalysts, whereas the yields of gas hydrocarbon and water vary separately from 5.6 wt % to 5.7 wt % and from 4.3 wt % to 7.6 wt %. Through comparison of these catalysts' yields of the liquid hydrocarbon products and theoretical values, we can safely conclude that almost all triglycerides in the jatropha oil were converted into hydrocarbons. It can also be found that the PtPd/Al₂O₃ catalyst has

Table 4. Yields and Component Properties of Liquid Hydrocarbon Products over Different Hydrotreatment Catalysts at $\text{LHSV} = 2$ h⁻¹, 3 MPa H₂, H₂/Feed (volume) = 600

catalyst	yields based on feedstock, wt %					
	PtPd/Al ₂ O ₃	catalyst A	catalyst B			
liquid hydrocarbon yield	81.2	83.9	83.8			
gas hydrocarbon yield	5.6	5.6	5.7			
water yield	4.3	7.5	7.6			
selectivity of different hydrocarbons in liquid hydrocarbon (C %)						
	PtPd/Al ₂ O ₃		catalyst A		catalyst B	
	normal	iso	normal	iso	normal	iso
C ₄	0.00	0.00	0.01	0.00	0.02	0.00
C ₅	0.00	0.00	0.05	0.00	0.06	0.00
C ₆	0.00	0.00	0.11	0.00	0.14	0.00
C ₇	0.03	0.00	0.22	0.00	0.23	0.00
C ₈	0.05	0.00	0.24	0.00	0.26	0.00
C ₉	0.04	0.00	0.31	0.00	0.33	0.00
C ₁₀	0.08	0.00	0.28	0.00	0.30	0.00
C ₁₁	0.05	0.00	0.20	0.00	0.21	0.00
C ₁₂	0.06	0.00	0.14	0.00	0.16	0.00
C ₁₃	0.05	0.00	0.13	0.00	0.14	0.00
C ₁₄	0.02	0.00	0.13	0.00	0.14	0.00
C ₁₅	13.92	0.00	7.61	0.06	7.89	0.16
C ₁₆	0.44	0.00	7.26	0.17	7.85	0.54
C ₁₇	81.38	0.21	37.31	3.19	36.89	4.26
C ₁₈	1.46	0.07	36.49	3.67	33.03	4.82
C ₁₈₊	2.13		2.41		2.59	
component properties of liquid hydrocarbon (C %)						
	PtPd/Al ₂ O ₃		catalyst A		catalyst B	
selectivity of C _{4–14}	0.39		1.83		1.98	
selectivity of C _{15–18}	97.48		95.76		95.42	
i-paraffin/ <i>n</i> -paraffin	0.003		0.078		0.111	
C ₁₅₊₁₇ /C ₁₆₊₁₈ ^a	48.42		1.01		1.06	

^aC₁₅₊₁₇/C₁₆₊₁₈: molar ratio of C₁₅H₃₂ and C₁₇H₃₆ to C₁₆H₃₄ and C₁₈H₃₈ in liquid hydrocarbon products.

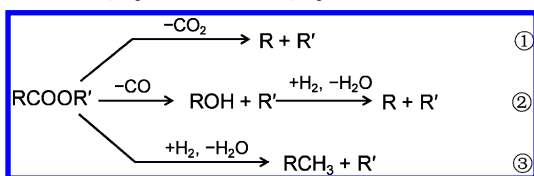
lower yields of water and total hydrocarbon than either of the other two NiMo catalysts. This fact results from the oxygen-removing pathway of PtPd/Al₂O₃ catalyst, which was primarily compiled with decarboxylation or decarbonylation and mainly CO, CO₂ formed, whereas the other two NiMo catalysts were executed primarily by hydrodeoxygenation and much water was formed. The formation of CO and CO₂ also means the loss of one carbon for hydrocarbon products.

As Table 4 shows, the hydrocarbon distribution of the liquid hydrocarbon products centered at the carbon number 15–18 over all three catalysts. This result occurs because of the main fatty acid component of feed is C₁₆ and C₁₈, which formed hydrocarbons of C₁₅, C₁₆, C₁₇, and C₁₈ by the three deoxygenation pathways described previously. The selectivity of C_{4–14}, which can be regarded as products of cracking reaction, decreases in the order catalyst B > catalyst A > PtPd/

Al₂O₃. The ratios of iso-paraffin and *n*-paraffin of the catalysts follow the same order as selectivity of C_{4–14}. As we all know, both hydrocracking and hydroisomerization reactions process essentially through the carbenium ion mechanism, in which acid properties of a support play a key role. Phosphorus is a promoter for NiMo/Al₂O₃ hydrotreating catalysts, and it has reported that addition of phosphorus increases the acidity of Al₂O₃.^{20,21} The addition amount of phosphorus in catalyst PtPd/Al₂O₃, catalyst A and catalyst B are respectively 0 wt %, 2.6 wt % and 5.8 wt % (Table 3). Although catalyst PtPd/Al₂O₃ has a different metal active site with catalyst A and catalyst B, we can still find that the yield of cracking and isomerization products increase with the additions of phosphorus. Consequently, the higher selectivity of C_{4–14} and ratio of *i*-paraffin and *n*-paraffin should be attributed to the higher acidity, which derived from the addition of phosphorus.

It is necessary to analyze the deoxygenation pathway of the reaction over different catalysts because it influences not only the distribution of liquid hydrocarbon products but also the H₂ consumption, which is an important issue from an industrial perspective. According to the referred reaction pathway of triglyceride deoxygenation, three deoxygenation pathways exist, as shown in Scheme 1. One mole of C_{*n*} (where *n* signifies the

Scheme 1. Three Deoxygenation Pathways of Vegetable Oil over NiMo/Al₂O₃ and PtPd/Al₂O₃



carbon number) fatty acid in the triglyceride generates a C_{*n*} hydrocarbon by hydrodeoxygenation (pathway 3) with two mole hydrogen consumed but generates a C_{*n*-1} hydrocarbon by decarbonylation (pathway 2) or decarboxylation (pathway 1) with one mole of hydrogen consumed or no hydrogen consumed, respectively. To investigate the selectivity of decarboxylation/decarbonylation and hydrodeoxygenation, the ratio of C₁₅ and C₁₇ to C₁₆ and C₁₈ was calculated. As Table 4 shows, the C₁₅₊₁₇/C₁₆₊₁₈ ratio of both NiMo catalysts (catalyst A and catalyst B) were similar and close to 1, but the ratio of PtPd/Al₂O₃ catalyst was 48.42. This result shows that the metal center strongly affects the reaction pathway and that the deoxygenation pathway of PtPd/Al₂O₃ catalyst was mainly decarboxylation/decarbonylation, whereas two NiMo/Al₂O₃ catalysts were executed primarily by the hydrodeoxygenation pathway. This result is also in agreement with results obtained from the yield of water over catalysts of two kinds. Previous works^{8,20,21} have also reported the deoxygenation pathway over

different catalysts. They found that NiMo catalyst was similar to CoMo but different to NiW catalyst, but did not explain the reason. Seen from a different perspective, hydrodeoxygenation and decarboxylation/decarbonylation can also be regarded as the cleavage of a C–O bond and C–C bond. Alcalá and co-workers reported that the rate constant for C–C bond cleavage in ethanol is higher than that for C–O bond cleavage on Pt at temperatures higher than about 550 K.²² This point is useful to explain the higher C₁₅+C₁₇ selectivity of PtPd/Al₂O₃ catalyst.

Some properties of liquid hydrocarbon products over the three catalysts are presented in Table 5, which shows that the liquid hydrocarbon products over the three catalysts are free of carboxylic acid (because of the extremely low acid number) and unsaturated hydrocarbon and that they have suitable density and viscosity and a quite high cetane index (corresponding to diesel oil). Even though these liquid products have had low-temperature fluidity, they can still serve as a high-performance additive for diesel oil. Moreover, the distillation properties of liquid hydrocarbon products over the three catalysts are shown in Table 6. As it can be seen, the fraction distilled from 270 to

Table 6. Simulated Distillation Results of Liquid Hydrocarbon Products over Different Catalysts

amount of distillation	boiling point (°C)		
	PtPd/Al ₂ O ₃	catalyst A	catalyst B
IBP	271	120	111
5%	276	268	266
10%	287	281	273
30%	290	298	297
50%	294	304	303
70%	298	312	311
90%	302	318	319
95%	306	324	323
EP	484	475	468

320 °C was the major distillation fraction over all catalysts, which is primarily alkanes ranging from C₁₅ to C₁₈. Some hydrocracking catalysts, such as NiMo/Al₂O₃-SiO₂,^{12,20} NiW/Al₂O₃-SiO₂,²³ NiMo/HY,²³ NiMo/HZSM-5²³ were reported for hydrotreating of vegetable oil to increase the selectivity of iso-alkanes, but these catalysts did not increase so much the selectivity of iso-alkanes but decreased the yield of diesel fraction (for Al₂O₃-SiO₂ based catalysts, iso-alkanes selectivity is less than 30%, but the yield of diesel fraction is less than 75%; for NiMo/HZSM-5 and NiMo/HY catalysts, the yield of diesel fraction is less than 50%). Due to the strong cracking activity, they are not considered as the suitable choice. Solid acid HZSM-5, HY, and Al₂O₃-SiO₂ are good supports choice for naphtha fraction isomerization but not for long-chain alkanes (C_{15–18}). Based on previous works,^{24–26} utilizing ZSM-

Table 5. Properties of Liquid Hydrocarbon Products over Different Catalysts

catalyst	density (g/cm ³ /15 °C)	dynamic viscosity (mPa·s/25 °C)	acid number (mg KOH/g)	cloud point (°C) ^b	cetane index ^c
diesel oil ^a	0.77–0.80	2–4.5	–	–	51–70
jatropha oil	0.91	21.17	8.48	–4	45
PtPd/Al ₂ O ₃	0.78	3.21	<0.1	20	93
catalyst A	0.78	3.25	<0.1	18	97
catalyst B	0.78	3.06	<0.1	16	96

^aCWA 15940:2009: automotive fuels—paraffinic diesel from synthesis or hydrotreatment requirements and test methods. ^{b,c}Cloud point and cetane index were determined according the ASTM D5773 and ASTM D4737.

22, SAPO-11, and AIMCM-41 as acid supports are considered to be studied more for deoxygenation and isomerization of vegetable oils in on step.

3.4. Effects of Reaction Temperature on Catalytic Performance. Performance of different temperatures over catalyst A was investigated at the condition of LHSV = 2 h⁻¹, P = 3 MPa, and H₂/oil = 600 mL/mL. Conversions of catalyst A at the four investigated temperatures were 100% because no oxygenates were determined in liquid hydrocarbon products. Figure 2 portrays the distribution of the liquid hydrocarbon

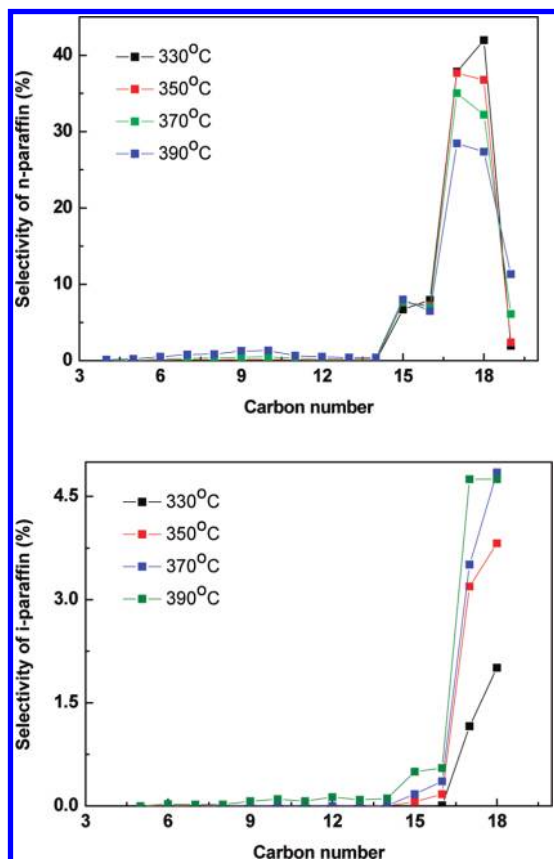


Figure 2. Carbon number distributions of liquid hydrocarbon products at different temperatures with catalyst A at LHSV = 2 h⁻¹, 3 MPa H₂, and H₂/feed (volume) = 600.

products at the four temperatures. The high reaction temperature has a small but positive influence on products selectivity. At low temperature, the hydrocarbon distribution of the liquid hydrocarbon products is very narrow (centered at the C_{15–18}) and the selectivity of i-paraffin is very low, which engenders the bad cold flow properties of the liquid hydrocarbon products. However, with increasing temperature, the hydrocarbon distribution becomes broader (light paraffin C_{4–14} was formed by cracking), and more iso-paraffin was produced by isomerization. Both iso-paraffin and partial light paraffin (C_{11–14}) are favorable products, which can improve the cold flow properties of the diesel fraction in liquid hydrocarbon products. To study the effect of the temperature on the deoxygenation pathway, Figure 3 shows the C₁₅₊₁₇/C₁₆₊₁₈ ratios of liquid hydrocarbon products over catalyst A at different temperatures. At temperatures of 330–390 °C, higher temperatures produced higher C₁₅₊₁₇/C₁₆₊₁₈ ratios. According to the preceding discussion (C₁₅ and C₁₇ are products of decarbox-

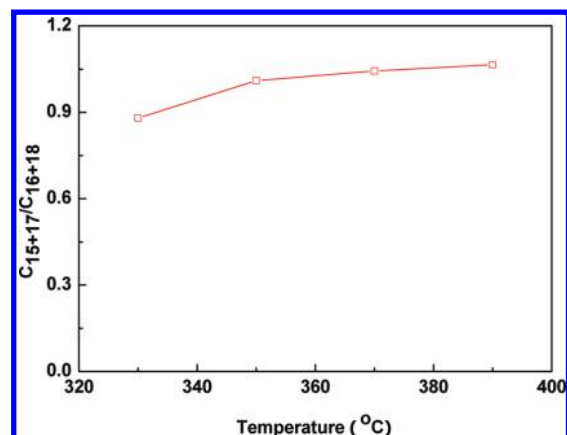


Figure 3. Effects of reaction temperature for deoxygenation pathway measured as C₁₅₊₁₇/C₁₆₊₁₈ ratios with catalyst A at LHSV = 2 h⁻¹, 3 MPa H₂, and H₂/feed (volume) = 600.

ylation/decarbonylation pathway, but C₁₆ and C₁₈ are products of hydrodeoxygenation pathway), we conclude that a high temperature is favorable for decarboxylation/decarbonylation pathway over catalyst A because the high temperature has a positive effect on cleavage of the C–C bond.

3.5. Long-Term Hydrogenation of Jatropha Oil. To investigate the lifetime and the effect of the reaction time, long-term experiments of 130 h were conducted over catalyst A at the condition of LHSV = 2 h⁻¹, P = 3 MPa, H₂/oil = 600 mL/mL, and T = 350 °C. Results show no activity loss found before reaction time of 120 h. Before the reaction time of 120 h the liquid hydrocarbon distributions at different reaction time were similar, but the deactivation of catalyst A was significant, and the liquid products became cloudy and included a suspension of white crystals from reaction time of 120 h (Figure 4). The

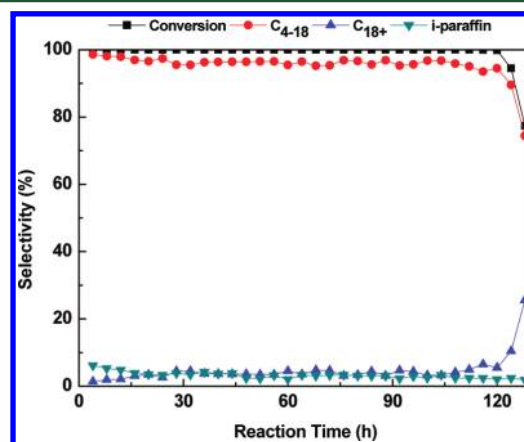


Figure 4. Conversion and the distribution of liquid hydrocarbon products as a function of the reaction time with catalyst A at LHSV = 2 h⁻¹, 3 MPa H₂, T = 350 °C and H₂/feed (volume) = 600.

fast deactivation of the catalyst after 120 h seems strange. However, we did the lifetime experiment twice and obtained the similar results. It is considered that the reduction of hydrogenation center and the fast coking create a vicious circle and lead to a sharp loss of activity. Meanwhile, the selectivity of iso-paraffin slowly reduced with the increasing reaction time because of the acidity centers were covered by coke. Increasing the reaction temperature was used to attempt to compensate the activity loss, but it failed. The specific surface area of the

spent catalyst was determined after pretreatment of 400 °C/vacuum for 1 h. Results show that the spent catalyst still has specific surface area up to 166 m²/g (compared with the fresh catalyst, it lost only 27 m²/g). Consequently, coke and hydrothermal instability are not the main causes of deactivation. It is known that the sulfides of NiMo have much higher activity than the oxides of NiMo for hydrogenation reactions. In the presulfided step, oxide catalyst is converted to sulfide catalyst as following reaction equation: NiO + MoO₃ + H₂S ↔ NiS_x + MoS₂ + H₂O.²⁷ However, this reaction is also a reversible reaction, which means that sulfide catalyst can be converted to oxide catalyst under suitable conditions. Due to the formation of 7.6 wt % water over catalyst A in hydrotreating of jatropha oil and the sulfur contained in products, sulfide catalyst conversion to oxide catalyst by the water formed in the reaction is regarded as the main cause of activity loss. To verify this perspective, the spent catalyst received regeneration treatment (calcined at air flow and 500 °C for 3 h first, then sulfided at 400 °C with a mixture of 5 vol % H₂S and 95 vol % H₂ flow for 3 h). Then, it was tested for catalyst performance. Results showed that the regenerated catalyst had the same catalytic performance, which well confirmed the deactivation cause presented above. Frequent regeneration would render the process very inefficient, and thus, co-adding trace sulfur agent to keep the catalyst in its active presulfided stage is considered to be a more feasible way to resolve the lifetime problem.²⁸ Sulfide catalyst was used in the experiment. Therefore, the sulfur eliminated from sulfide catalyst and dissolved into products should be considered. From the start to the reaction of 120 h, all liquid hydrocarbon products were collected and mixed. The sulfur content of the mixed liquid hydrocarbon products, determined using a total sulfur analyzer (TS-100; Mitsubishi Chemical Analytec Co. Ltd.), was 7.6 ppm.

4. CONCLUSIONS

Hydrotreatment of nonedible jatropha oil was performed on a PtPd/Al₂O₃ catalyst and two sulfided NiMoP/Al₂O₃ catalysts. The main conclusions derived from this work are the following: Both PtPd/Al₂O₃ catalyst and two sulfided NiMoP/Al₂O₃ catalysts show good performance: significantly higher yield range 81.2–83.9 wt % of liquid hydrocarbon products was achieved for all catalysts. The liquid hydrocarbon products over the three catalysts are almost free of nitrogen, sulfur, carboxylic acid, and unsaturated hydrocarbon. Moreover, they have suitable density and viscosity and quite high cetane index. They are high-performance additives for diesel oil. The oxygenation removal pathway of jatropha oil over PtPd/Al₂O₃ catalyst is primarily compiled with the lower H₂-consumption pathway—decarboxylation or decarbonylation—whereas the other two sulfided NiMo catalysts are primarily executed by hydrodeoxygenation. Deactivation of catalyst A was found from reaction time of 120 h. Sulfide catalyst conversion to oxide catalyst is regarded as the main reason for deactivation. The deactivated catalyst can be reused after regeneration treatment.

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Notes

The authors declare no competing financial interest.

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