

Effect of Biomass Feedstocks on the Production of Hydrogenated Biodiesel

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Abstract—Hydrogenated biodiesel is one of the most promising renewable fuels. It has many advantages over conventional biodiesel, including higher cetane number, higher heating value, lower viscosity, and lower corrosiveness due to its absence of oxygen. From previous work, Pd/TiO₂ gave high conversion and selectivity in hydrogenated biodiesel. In this work, the effect of biomass feedstocks (i.e. beef fat, chicken fat, pork fat, and jatropha oil) on the production of hydrogenated biodiesel over Pd/TiO₂ has been studied. Biomass feedstocks were analyzed by ICP-OES (inductively coupled plasma optical emission spectrometry) to identify the content of impurities (i.e. P, K, Ca, Na, and Mg). The deoxygenation catalyst, Pd/TiO₂, was prepared by incipient wetness impregnation (IWI) and tested in a continuous flow packed-bed reactor at 500 psig, 325°C, H₂/feed molar ratio of 30, and LHSV of 4 h⁻¹ for its catalytic activity and selectivity in hydrodeoxygenation. All feedstocks gave high selectivity in diesel specification range hydrocarbons and the main hydrocarbons were n-pentadecane (n-C15) and n-heptadecane (n-C17), resulting from the decarbonylation/decarboxylation reaction. Intermediates such as oleic acid, stearic acid, palmitic acid, and esters were also detected in minor amount. The conversion of triglycerides in jatropha oil is higher than those of chicken fat, pork fat, and beef fat, respectively. The higher concentration of metal impurities in feedstock, the lower conversion of feedstock.

Keywords—Hydrogenated biodiesel, hydrodeoxygenation, Pd/TiO₂, biomass feedstock

I. INTRODUCTION

At present, the energy consumption has surged due to the rise of the world population which led to the sudden decrease in energy supply especially in fossil fuel. There are many concerns with the use of fossil fuel, including limited fuel reserves, unpredictable crude oil price, and unwanted gas emission, e.g. SO_x and NO_x. The number one blame of these concerns goes to the emission of diesel engines from automobiles and industrial equipments that use fuel. From these problems, the development of alternative and sustainable energy is important to satisfy the demand of energy consumption, as well as to reduce the unwanted gas emission. There are several sustainable alternative energysources, including hydropower, thermal energy, wind energy, solar energy, biomass, and biofuels.

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The most prominent of these energies which can compensate diesel fuel is biodiesel as it has same performance as regular fuel engines, emit less pollution, and can be produced from renewable raw materials.

Biodiesel is referred to the fatty acid methyl ester (FAME) or mono-alkyl esters of long-chain fatty acids derived from vegetable oils or animal fats via transesterification process. Biodiesel is biogradable and produces lower level of air pollutants than fossil fuels. Notwithstanding, biodiesel price is usually higher than the fossil fuels and it has some undesired properties, e.g. high viscosity and low heating value which may cause engine problems especially at low temperature. These properties are the result of the content of oxygen in the product. However, the hydrocarbon like biodiesel which is called “renewable diesel”, “green diesel”, or “hydrogenated biodiesel” is also available.

The hydrogenated biodiesel can be produced via the hydrodeoxygenation of triglyceride-containing feedstocks at elevated temperature and pressure (300-450 °C and 500-2000 psia) in the presence of conventional hydrotreating catalysts [11]. There are many advantages of hydrodeoxygenation over transesterification, including higher cetane number and heating value, low viscosity, and less pollutant emission due to its absence of oxygen atom in its molecule.

There have been many research works focused on biodiesel and biodiesel production from vegetable oil (i.e. palm oil, corn oil, and jatropha oil) [2,3,7,10] and some research focused on the effect of various impurities in feedstocks which reduce the activity of hydrotreating catalysts [9,12]. However, the report on the utilization of animal fats, which are considered as the alternative feedstocks, is still limited.

The objective of this research is to study the effect of feedstocks (i.e. jatropha oil, beef oil, pork fat, and chicken fat) on the deactivation of 1 wt% Pd/TiO₂ catalysts for production of hydrogenated biodiesel. The activity and selectivity of the catalysts and major impurities in feedstocks will also be investigated.

II. EXPERIMENTAL

A. Materials

Dodecane [CH₃(CH₂)₁₀CH₃, 99.9 % purity, Merck] was used as a solvent of all feedstocks in this research. Palladium(II) nitrate hydrate (Pd(NO₃)₂.xH₂O, 99.9 % purity, Aldrich) and commercially titanium dioxide (TiO₂) power, Degussa P-25, were used as metal precursor and support, respectively.

B. Catalyst Preparation

1 wt% palladium supported titania catalyst was prepared by using incipient wetness impregnation method. The TiO₂

support was initially dried at 110 °C overnight and calcined at 500 °C for 4 hours. The TiO₂ was then impregnated with the aqueous solution of Pd(NO₃)₂. Distilled water was used as solvent for preparing the metal precursor solutions. The impregnated catalyst was then dried at 110 °C overnight followed by calcined at 500 °C for 6 h. The prepared catalyst was finally pelletized, mash and sieved to the particle size 20/40 mesh.

C. Catalytic Characterization

The surface area of the fresh catalyst was measured by Brunauer-Emmett-Tellett (BET) surface area analyzer (Quantachrome/Autosorb 1). The sample was first outgassed to remove the humidity and volatile adsorbents adsorbed on surface under vacuum at 150 °C for 4 h prior to the analysis. Then, N₂ was purged to adsorb on surface, and the quantity of gas adsorbed onto or desorbed from their solid surface at some equilibrium vapor pressure by static volumetric method was measured. The solid sample was maintained at a constant temperature of the sample cell until the equilibrium was established. This volume-pressure data was used to calculate the BET surface area.

Thermogravimetric analyze was performed by using a Perkin Elmer Pyris Diamond TG/DTA to determine the thermal decomposition behavior and to obtain suitable calcination temperature of the catalyst. The dried sample of approximately 5-15 mg was heated from 50 to 800 °C with a temperature increase rate of 10 °C/min in a static air atmosphere.

Temperature programmed oxidation (TPO) was carried out to determine the amount and characteristics of coke formed on the spent catalysts. TPO profiles of the spent catalysts were performed in a continuous flow of 2% O₂/He while the temperature was linearly ramped to 1073 K with a heating rate of 12 K/min. The 30 mg of sample was placed in a ¼" quartz fixed bed reactor. The CO₂ produced by the oxidation of coke was further converted to methane over 15% Ni/Al₂O₃ catalyst in the presence of hydrogen at 673 K. The methane obtained was analyzed online by a FID detector. The amount of oxidized coke was calibrated using 100 pulses of pure CO₂.

D. Catalytic Activity Testing

The experiment was carried out in a high pressure fixed bed continuous flow reactor. First, the prepared catalysts were placed in the reactor and reduced by flowing hydrogen at 200 psig, 200 °C for 3.5 h. The hydrodeoxygenation was conducted at 325 °C, 500 psig, LHSV of 4 h⁻¹ and H₂ to feed molar ratio of 30. Then, the stream of 30 vol.% feedstock in n-dodecane was fed to the reactor using a high pressure pump. The flow of carrier gas and the reaction pressure was controlled by a mass flow controller and a back pressure regulator, respectively. The liquid product was collected in a stainless steel cylinder trap at the bottom of reactor.

E. Feed and Product Analysis

All feedstocks were analyzed for fatty acid compositions by gas chromatography with flame ionization detector (GC/FID) in accordance with a modified AOAC 996.06 method. The

liquid products from the hydrodeoxygenation were dissolved in pyridine and silylated with N,O-bis (trimethylsilyl)-trifluoroacetamide, BSTFA (99 % purity, ACROS), to improve the chromatographic behavior and then were analyzed by an Agilent Technology 7890A gas chromatograph equipped with a FID detector. Eicosane C₂₀H₄₂ (99 % purity, ACROS), was added as internal standard for quantitative calculations.

All feedstocks were analyzed for trace amounts of impurities (i.e. P, K, Ca, Na, and Mg) by ICP-OES (inductively coupled plasma optical emission spectrometry). The residual substance from burning feedstock at 600 °C for 150 min was dissolved in HNO₃ at 70 °C for 20 min and then filtered and diluted to 100 ml. Then the sample solution was fed by peristaltic pump into a nebulizer where it is changed into mist and introduced directly inside the high temperature plasma flame of about 7000 K. The intensity of the emission is indicative of the concentration of the element within the sample.

III. RESULTS AND DISCUSSION

A. Catalytic characterization

Textural properties of the TiO₂ support and Pd/TiO₂ catalysts (surface area, total pore volume, and mean pore diameter) obtained from Brunauer-Emmett-Tellett surface area analyzer are shown in Table 1. The surface area of TiO₂ (Degussa P 25) is 50.50 m²/g which close to the given property (50 m²/g). The surface area of prepared catalyst is lower when compared with the TiO₂ support due to the deposit of the metal on the support surface.

TABLE I
TEXTURAL PROPERTIES OF THE CATALYST

Catalyst	Surface area (S _{BET}) (m ² /g)	Total pore volume (cm ³ /g)	Mean pore diameter (nm)
P25- TiO ₂	50.50	0.230	18.50
P25-IWI	48.80	0.228	18.70

Thermogravimetry and differential thermal analysis (TG-DTA) was used to study the thermal decomposition behavior and the suitable calcination temperature of the catalyst. Fig. 1 shows TG-DTA curve of 1 wt% Pd/TiO₂ catalyst prepared by incipient wetness impregnation method. The DTA curve showed two main exothermic regions. The first exothermic peak at temperature lower than 150 °C is contributed to the removal of physisorbed water molecules. The exothermic region between 150 and 500 °C corresponds to the removal of organic remnants and chemisorbed water molecule, respectively [6]. The TG result reveals that the weight losses end at a temperature of approximately 500 °C. Therefore, the appropriate calcination temperature for Pd/TiO₂ catalyst is 500 °C.

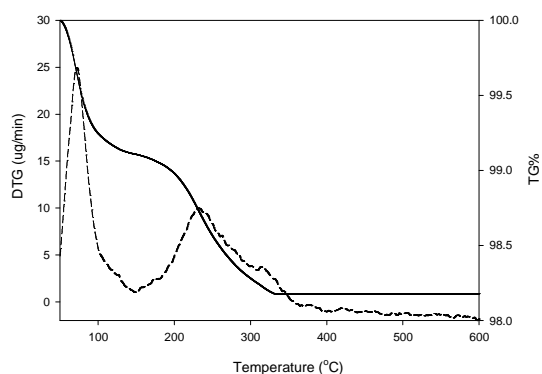


Fig. 1 TG-DTA profile of 1 wt% Pd/TiO₂ catalyst prepared via incipient wetness impregnation method (IWI)

The amounts of coke deposit on spent catalysts (after 7 TOS) are illustrated in Table II. The peaks observed at temperatures below 400 °C represented the weakly coke deposit on the support, while peaks above 400 °C, indicated the strongly coke deposit. The peak of coke deposit on the spent catalyst from all feedstocks observed at temperature about 350 °C which indicated to the weakly coke.

TABLE II
AMOUNT OF CARBON DEPOSIT ON THE SPENT CATALYST

Feedstocks	Carbon deposit (wt.%)
Beef fat	10.42
Chicken fat	6.26
Pork fat	8.69
Jatropha oil	10.47

B. Feed and product analysis

The fatty acid compositions of all feedstocks were also analyzed followed the AOAC 996.06-GC method. From the results as shown in Table III, the main fatty acids in all feedstocks are palmitic acid (C16) and oleic acid (C18).

TABLE III
FATTY ACID COMPOSITION OF FEEDSTOCKS

Oil or Fat	Saturated			Mono unsat.	Poly unsat.
	Myristic Acid C14:0	Palmitic Acid C16:0	Stearic Acid C18:0	Oleic Acid C18:1	Linoleic Acid C18:2
Beef	3.3	26.13	16.38	40.71	1.26
Chicken	0.49	20.08	4.34	33.78	31.52
Jatropha	0.06	13.81	6.89	45.84	31.98
Pork	1.84	21.44	9.4	39.23	18.5

The inductively coupled plasma optical emission spectrometry was used to detect the amount of trace elements which are the main impurities in feedstocks. The metals investigated in this work are Mg, Na, P, Ca and K. The amount of metals in each feedstocks are shown in Table IV. From the result, all biomass feedstocks contain the significant concentrations of impurities.

The impurities were classified into two groups, alkali (Mg, Na, K and Ca) and phosphorus. Alkalis are the natural impurities in feedstock and phosphorus is the representation of phospholipids. The balance between the cations (alkali) and anions represented by the phosphate anion originating from phospholipids is also studied. Their balance can be seen from the compensation between milliequivalent of cations (M eq.) and concentration of P (mmol/kg) as shown in Table IV. Milliequivalent can be obtained from equation (1), where anion charge was equal to -2 , as the phosphate group is bound to the glycerol backbone in phospholipids.

$$Meq. = \frac{\sum (cation \cdot charge \times cation \cdot conc.) / cation \cdot atomic \cdot weight}{|anion \cdot charge|} \quad (1)$$

The most pronounced imbalance was observed for beef fat which showed the worst performance (Table V). In the case of imbalance between cations and anions the deactivation rate will increase with the increasing concentration of impurities. In the specific case when the concentration of cations of alkalis and phosphate anion are in balance, deposits will be formed that will cause plugging of the reactor [12].

C. Catalytic activity

To study the catalytic activity and selectivity in deoxygenation over Pd/TiO₂ catalyst, the production of hydrogenated biodiesel from beef oil, chicken fat, pork fat, and jatropha oil were conducted at 325°C, 500 psig, liquid hourly space velocity (LHSV) of 4 h⁻¹, and H₂/feed molar ratio of 30 for 7 hours. The liquid product was analyzed by gas chromatograph. Table V summarizes the conversions of beef fat, chicken fat, pork fat and jatropha oil and the product selectivity at various times on stream.

TABLE IV
CONCENTRATIONS OF MAIN IMPURITIES IN EACH FEEDSTOCKS

Feed	Mg (ppm)	Na (ppm)	K (ppm)	Ca (ppm)	P (ppm)	M eq. (mmol/kg)	P (mmol/kg)
Beef fat	2.14	54.20	7.03	25.01	16.61	1.98	0.54
Chicken fat	1.63	5.70	2.32	14.06	8.31	0.57	0.27
Pork fat	1.84	5.14	2.16	14.68	10.01	0.58	0.32
Jatropha oil	3.62	4.43	1.98	19.44	20.28	0.76	0.65

The results showed that all biomass feedstocks can be converted to long chain hydrocarbons in diesel specification range (C15-C18). The main products obtained from all feedstocks were n-pentadecane (n-C15) and n-heptadecane (n-C17), resulting from the decarbonylation/ decarboxylation reaction which one carbon atom is removed out of original fatty acids in each oil molecule. The intermediates such as stearic acid, oleic acid, palmitic acid and the others products like tridecane (C13) and tetradecane (C14) are also detected.

From the results, jatropha oil feedstock tends to give the highest conversion followed by chicken fat, pork fat and beef fat, respectively, while the selectivity toward the product in diesel range hydrocarbons (C15-C18) is not significantly difference for all feedstocks. The conversion (Table V) may be affected by the impurities in each feedstock (Table IV). The higher concentration of metal impurity tended to give the lower conversion which may result from their deposition on catalyst surface.

In addition, the higher concentration of phosphorus tended to give the higher coke deposition which may resulting from oligomerization reactions catalyzed by phosphoric acid from decomposition of phospholipids.

IV. CONCLUSIONS

In this work, the production of the hydrogenated biodiesel from biomass feedstocks over 1 wt% Pd/TiO₂ catalyst has been investigated. All feedstocks can be converted into desired products, hydrogenated biodiesel (C15-C18) via deoxygenation reaction. The main products of all feedstocks are n-pentadecane (n-C15) and n-heptadecane (n-C17) resulting from the decarboxylation/decarbonylation reaction. The conversion of triglycerides in jatropha oil is higher than those of chicken fat, pork fat, and beef fat, respectively. The higher concentration of metal impurities in the feedstock, the lower conversion of triglycerides was due to the deposition of impurities on the catalyst surface. Moreover, the higher concentration of phosphorus gave the higher coke deposition due to the oligomerization reactions catalyzed by phosphoric acid.

TABLE V
CONVERSION AND PRODUCT SELECTIVITY FROM HYDRODEOXYGENATION OVER Pd/TiO₂ CATALYST

Feedstock	Beef fat			Pork fat			Chicken fat			Jatropha oil		
	2	4	6	2	4	6	2	4	6	2	4	6
Time on stream (h)	2	4	6	2	4	6	2	4	6	2	4	6
Conversion	40.61	33.70	24.24	56.27	50.08	46.21	51.81	41.32	37.85	61.97	56.41	56.77
Selectivity (%)												
<i>Total C15-C18</i>	56.18	50.50	52.59	59.61	54.98	52.46	58.61	51.75	47.70	52.80	49.79	49.23
n-C15	14.08	11.17	12.53	14.19	12.98	12.20	14.94	13.22	12.37	8.25	7.48	7.33
n-C16	4.67	5.31	4.69	2.61	2.50	2.54	2.16	1.86	1.57	1.12	1.29	1.44
n-C17	29.55	24.45	27.05	37.34	34.29	32.41	37.01	32.77	30.53	39.44	36.30	35.19
n-C18	7.87	9.56	8.32	5.47	5.21	5.31	4.49	3.89	3.24	4.00	4.72	5.27
<u>(C15+C17)</u> <u>(C16+C18)</u>	3.48	2.39	3.04	6.38	6.13	5.68	7.80	7.99	8.92	9.32	7.29	6.33
<i>Intermediates</i>	39.25	45.05	42.88	38.59	43.25	45.75	40.08	47.08	51.14	46.62	49.64	50.18
hexadecanol	0.00	0.00	0.00	1.17	1.10	1.06	0.65	0.65	0.52	0.00	0.00	0.00
palmitic acid	6.80	7.70	7.22	4.35	4.76	5.14	5.57	6.97	7.96	3.74	3.67	3.71
oleic acid	2.47	2.51	2.65	11.94	13.26	13.72	13.39	15.93	17.73	17.54	16.25	16.52
stearic acid	15.10	16.59	16.22	1.84	2.18	2.30	1.64	2.81	3.18	2.05	3.25	3.53
esters	12.50	14.65	13.90	17.43	19.86	21.92	16.82	17.87	18.84	23.29	26.47	25.60
diglycerides	2.38	3.60	2.90	1.85	2.09	1.62	2.01	2.86	2.91	0.00	0.00	0.82
<i>Others</i>	4.57	4.45	4.53	1.90	1.79	1.59	1.31	1.17	1.16	0.58	0.57	0.58

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