

Development of one-step jet fuel blend using solid acid catalysts

Susanta Mohapatra,^a Reza Hemeyari,^a Ali Manesh^{a*} and Mano Misra^b

^aAmerican Science and Technology, 6445 Packer Dr, Wausau, WI 54401

^bUniversity of Utah, 135 South 1460 East/ Room 412 William Browning Building
Salt Lake City, UT 84112

AM: Ph. 715.845.0200; Fax: 715.845.7200; email: am@amsnt.com

MM: Ph. 801.581.6386; email: Mano.misra@utah.edu

ABSTRACT

Deoxygenation of used vegetable oil over several microporous and mesoporous catalysts has been investigated in this work. Optimization of reaction conditions with rapid catalyst screening were performed to achieve a goal to make liquid fuel with characteristics with JP8 fuel. Mild acidic catalysts such as SBA15 and activated carbon are excellent catalysts for the selective decarboxylation of used oil to linear hydrocarbons. On the other hand, super-acid WZr absed catalysts can perform simultaneously decarboxylation, cracking and cyclization reactions in a single step. The end product was free of oxygen, nitrogen and liquid till -20-30F with a gross energy value more than 19-20K Btu/lb.

Keywords: decarboxylation, JP8, used vegetable oil, heterogeneous solid acid catalyst.

1 INTRODUCTION

Fossil fuels have been the main source of energy and their use has been steadily increasing. The Energy Information Administration (EIA) has projected that the world marketed energy consumption will grow by 57 percent over the 2004 to 2030 period and will reach 702 quadrillion Btu. Consumption of liquid fuels has been steadily increasing in the United States and it is predicted that the total consumption grow at an average annual rate of 0.4 percent, from 20.7 million barrels per day in 2006 to 22.8 million barrels per day in 2030. Consumption of transportation fuels is predicted to have the highest growth and will increase from 68 percent in 2006, to 73 percent in 2030. The growth in transportation energy use is expected to be led by greater demand for aviation fuel. Aviation fuels (AF) (i.e., jet fuels) are a complex mixture of C8 to C17 organic compounds and are presently derived from the kerosene fraction of petroleum (crude oil) distillation as well as hydroprocessing of heavier fractions. JP-8 is another aviation fuel and similarly is a kerosene-based turbine fuel, very similar to the commercially produced Jet A and Jet A-1 fuels used by commercial airlines worldwide. JP-8 burning characteristics are very similar to diesel fuel and they burn neither hotter nor slower than diesel fuel and have a particularly low freezing point of 47 degrees Celsius

below zero (the temperature at which all wax crystals in the fuel disappear upon warming). JP-8 fuel mainly comprises hydrocarbons with carbon number ranging from 8 to 16 and a certain amount of aromatics. There is great interest to produce JP8 fuel from renewable feedstocks like triglycerides [1-4].

On the molecular level, conversion of triglycerides present in plant oils to jet fuel range hydrocarbons will involve the cleavage of the three chain molecules to single chain molecules, removal of ester linkages via deoxygenation including decarbonylation, decarboxylation and reduction, and subsequently in order to improve cold flow properties, such as freezing point and viscosity, isomerization of straight chain hydrocarbons to branched ones. UOP LLC and Eni S.p.a. of Italy jointly developed an ecofriendly process, in which triglycerides and/or free fatty acid feedstock are hydrogenated to produce paraffins and subsequently the resulting paraffins are isomerized to create a high quality hydrocarbon known as green diesel or green jet fuel dependent on the fuel product desired. Similarly, in another industrial NExBTL process commercialized by Neste Oil, the vegetable oils are first hydrogenated and deoxygenated over conventional hydrotreating catalysts. The resulting n-paraffins then undergo mild isomerization over an acidic catalyst to produce isoparaffins with improved cold flow properties. While the processes are very practical and utilize existing equipment present in most refineries, conventional hydrotreating catalysts are used in the form of metal sulfides which usually need certain amounts of sulfur compounds present in the feed to maintain the active phases and the resulting product may contain certain quantity of sulfur if produced from sulfided hydrotreating catalysts.

In this work we will discuss the conversion of used vegetable oil to JP8 fuel using solid acid. The developed catalyst performs deoxygenation, cracking and isomerization reaction in a single step.

2. MATERIALS AND METHODS

The restaurant oil was purified by centrifuge (1000 rpm, 70C, 30 min) followed by boiling (110 C for 1h). This process removes the water and suspended solid particles.

FFA content in the used oil was found to around 15% (analyzed by GCMS after functionalizing the FFAs with BSTFA). Fatty acid composition was mainly C18 and C16. Mesoporous silica materials (SBA15) were prepared by sol-gel process. Al (Si/Al=30) and Sn/SBA15 (Si/Sn =30) were also prepared for a comparison. Several metals such as Pt, Pd and Ni were loaded on the catalyst support by an incipient wetness process. Super-acids WZr and LaCeZrO₂ were provided by MEL Chemicals. For a comparison several commercial strong-acid supports such as Silica Alumina (SASOL) and alumina; weak acidic supports diatoms; and basic hydrotalcite and CaO supports were evaluated.

In one example of metal loaded catalyst preparation: 5%Pd/WZr catalyst was prepared as follows: 10g of WZr was calcined at 800 C for 3h. The calcined sample was then activated at 200 C for 3 h for the removal of adsorbed water molecules. 5wt % Pd was loaded into this activated support by the incipient wetness process. An aqueous solution of palladium nitrate was prepared by mixing 1090 mg of Pd nitrate in 20 g of DI water. The prepared Pd solution was added drop wise to the activated support. The impregnated sample was room dried (30 min), oven dried (180 C, 1h) and then calcined (to remove the nitrate) at 400 C for 1h. This process was repeated twice to impregnate rest of the stock solution. Finally, the sample was calcined at 800 C for 1h (air). All other metal supported catalysts were prepared by slightly changing the above condition.

Catalytic deoxygenation reactions were carried out in a semi batch reactor with continuous flow of H₂ (40-100 ml/min). Catalysts were in situ reduced under hydrogen at 300-375 C for 1-3h. Catalyst loading, type of solvent, temperature, pressure, reaction atmosphere and the suitable catalyst were optimized by a rapid screening process. After the reaction, solid catalyst and products were separated by gravity filtration. When the product was liquid warm filtration was carried out. 100 mg of this product was mixed with 1mL of dodecane and 1mL of chloroform for GC/MS analysis. For a comparison HPLC was also performed.

3. RESULTS AND DISCUSSION

From rapid screening three supports Activated carbon, LaCeZrO₂ and WZr were identified as the best catalyst for the name reaction. All other supports showed 25-35% conversion so LaCeZrO₂ and WZr based catalysts were further screened.

Decarboxylation of used oil using (5%Pd/C).

2 g of 5%Pd/C was used for the deoxygenation of used oil (18.5 g) at 340 C for 2h under H₂ atmosphere (250 psi, continuous flow). 16 g of Dodecane was used as a solvent. After the reaction, 32 g products were collected, which is 87.7% mass balance (solid+liquid, no gas was collected).

Catalyst and products were separated by gravity filtration. 100 mg of this product was mixed with 1mL of dodecane and 1mL of chloroform for GC/MS analysis. GC results showed that more than 99% conversion (combined TGs and FFAs) with more than 78% heptadecane selectivity (Table 1). The high percentage of C17 in the product stream compared to C18 confirms that decarboxylation dominates over deoxygenation reaction [5].

Table 1: Normalized product selectivity.

<i>Catalyst 5%Pd/AcC</i>	
Products	Selectivity, %
<i>pentadecane</i>	9.5
<i>hexadecane</i>	0.9
<i>heptadecane</i>	78.8
<i>octadecane</i>	4.8
<i>nonadecane</i>	1.0
<i>heneicosane</i>	1.5
<i>stearic acid</i>	1.87
<i>others</i>	1.45

Decarboxylation of used oil using 10%Ni/LaCeZrO₂:

Fig. 1 shows the formation of C17 (heptadecane) with time. The figure indicates that up to 90 min the formation of C17 is linear and after that the rate of conversion increases. This might be due to in the first 90 min, two reactions take place: first, formation of FFA from triglycerides and second, decarboxylation of FFA to C17. However, after 90 min, the conversion of TG to FFA completes and only decarboxylation takes place. Overall, at the end of 2h, more than 95% conversion was noticed. Heptadecane is the major product from the decarboxylation of C18 free fatty acid (formed from the degradation of triglycerides). Pentadecane is the second major product. Around 1% octadecane was also formed by the deoxygenation of C18 free fatty acids. From the product distribution, it is found that both decarboxylation and deoxygenation took place using Ni/LaCeZrO₂ catalyst. This catalyst behaves similar to activated carbon based catalyst. This catalyst behaves similar to activated carbon based catalyst. The advantage of this support is its better recyclability than activated carbon.

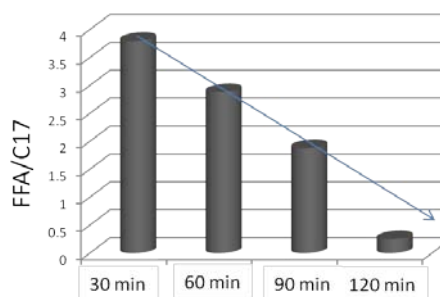


Fig. 1. Formation of C17 with increasing reaction time using Ni/LaCeZrO₂ catalyst.

Decarboxylation of used oil using 5%Pd/WO₃-ZrO₂.

GCMS showed 95-98% conversion with more than 90% linear hydrocarbon selectivity in 2h reaction, which is much lesser than many reported catalysts [6]. Linear hydrocarbons (C15, C17) are the major products (from the decarboxylation reaction). Cyclic and aromatic compounds were observed in all the reaction products using WZr as a catalyst (Figure 2). Presence of this product indicates that this catalyst not only produces hydrocarbons but also helps in the cyclization of linear alkanes. In addition to these, branched chain hydrocarbons were also observed in the product stream. Activity of this catalyst at 500 psi was almost similar to that of at 250 psi. At higher pressure more light hydrocarbons (<C13) formed. Activity of this catalyst was reduced once the reaction pressure was reduced from 250 psi to 150 psi, at lower reaction pressure more FFAs were observed. However, at lower pressure the reaction can be run for 3h to achieve the activity comparable to the activity at 250 psi. When the reaction temperature increased to 375 C (250 psi pressure), the conversion was more than 95% and in the product distribution 20-30% lower chain hydrocarbons (in the gasoline range) were observed. This indicates that at higher temp, cracking reactions are favorable. Reducing the Pd loading to 3% (340 C and 250 psi H₂) showed 90-92% conversion. In the product distribution, 88-90% hydrocarbon and 10-12 % free fatty acids (intermediates) were observed. Adding 0.5% Pt to this catalyst did not give any advantages over 5%Pd/WZr. Conversion was around 90% compared to 95% using only 5%Pd/WZr.

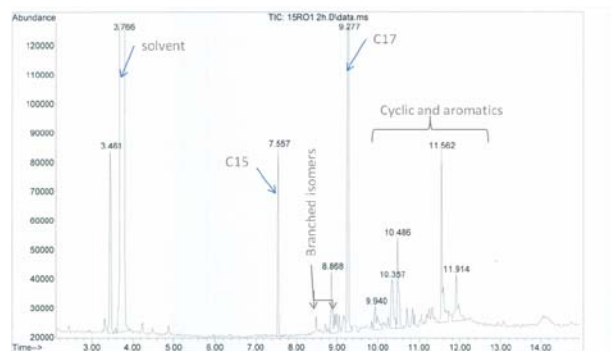


Figure 2: GC profile of the hydrocarbon products obtained from used restaurant oil. Deoxygenation, cracking and isomerization reactions take place in a single step reaction.

Decarboxylation using diesel as a solvent:

Decarboxylation of used oil was evaluated using diesel as a solvent. The objective is to use a cheaper and readily available solvent than dodecane. Under similar reaction conditions, the reactions using diesel showed similar activity and product selectivity compared to dodecane as solvent. Due to the addition of linear hydrocarbons and branched chain hydrocarbons (from the decarboxylation

reaction) the properties of diesel is closer to JP8 fuel. Every gallon of diesel produces 1.7-1.9 gallons of JP8 range fuel. It burns similar to the diesel fuel. A comparison of product distribution using the selected catalysts are listed in the table 2.

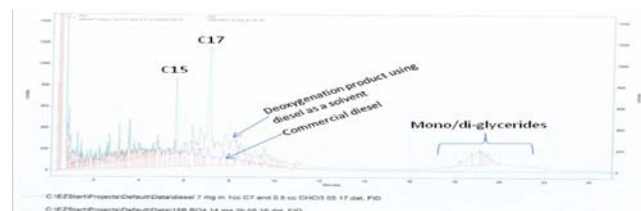


Figure 3: GC profile of commercial diesel and the JP8 range fuel produced using diesel as a fuel.

Table 2. Final product distribution based on GC analysis:

Catalyst	Used oil	Reac ⁿ time	Products				Total Hydrocarbon yield	Selectivity
			C17	C13-C16	C17 isomers	Cyclic and Aromatics		
5%Pd/C	18.5g	2h	8.8g	1g	-	-	9.8g	53
10%Ni/LaCeZrO ₂	4g	1.5h	1.2g	0.65g	-	-	1.85g	46
5%Pd/WZr	12g	2h	3.7g	0.67g	0.45g	1.76g	6.59g	55
5%Pd/WZr	12g	3h	5.8g	1.05g	0.77g	2.54g	10.16g	84

Final Product Analysis:

Elemental analysis showed ~100% deoxygenation took place in 1-3 hours of reaction. The product is liquid up to -20(-)-30F, which is very close to JP8 fuel requirement. The higher heating value of the product was identified as 19K btu/lb, which is comparable to JP8 fuel (table 3).

Table 3: calorific value of JP8 fuel range prepared by the decarboxylation of used vegetable oil.

sample	Btu/lb
Oil+diesel (1:1 by wt)	18,088
Deoxygenation product using diesel as solvent	19,433
Deoxygenation product using dodecane as solvent	20,017
Compared to various other fuels	
JP8	18,400 (gross)
diesel	19,300
gasoline	20,400

As can be seen from the table 4 that complete decarboxylation was achieved in these reaction. The H/C ratios are improved after the upgrading process. Products using diesel gives lower H/C ratio compared dodecane as it contains more aromatics than the reaction mixture obtained using dodecane as a solvent. Comparing these results with commercial fuels (diesel and JP8), the H/C ratio of these products are close to these commercial fuels.

Table 4. C/H/N/O analysis of the JP8 fuel range prepared by the decarboxylation of used vegetable oil.

sample	C (wt%)	H (wt%)	H/C(atom)	O (wt%)	N
Used oil	77.59	11.69	1.8	10.2	~0
dodecane and used oil (1:1 by wt)	79.31	13.62	2.06	4.83	~0
Deoxygenation product using dodecane as a solvent	84.87	14.89	2.1	0.05	~0
Used oil + diesel (1:1 by wt)	82.36	11.46	1.67	4.54	0.01
Deoxygenation product using diesel as a solvent	86.49	12.85	1.78	-0.21	~0
Comparison with other fuels					
diesel			1.916	-	-
JP8	86.07	13.7	1.91		

4. CONCLUSIONS

Decarboxylation of used vegetable oil to hydrocarbon fuel was carried out using several solid acid catalysts. LaCeZrO₂ and WZr were found to be the best catalysts for this application. Ni and Pd loaded catalysts not only did decarboxylation but also performed as isomerization and cyclization catalyst. The catalysts and reaction conditions are optimized so that a Jp8 kind fuel can be obtained from used vegetable oil in a single step reaction. More than 95% conversion and high hydrocarbon selectivity was obtained. The product showed high energy value comparable to commercial JP8 fuel.

5. REFERENCES

[1]. L. Li, E. Coppola, J. Rine, J.L. Miller, D. Walker, Energy & Fuels 24, 1305-1315, 2010.

[2] T. Morgan, D. Grubb, E. Santillan-Jimenez, M. Crocker, Top. Catal. 53, 820-829, 2010.

[3] T.V. Choudhary, C.B. Phillips, Appl. Catal. A 397, 1-12, 2011.

[4] S. Mohapatra, T. Morgan, E. Santillan-Jimenez, M. Crocker, Extended Abstract 22nd North American Meeting, Detroit, MI, June 2011.

[5] B. Donnis, R.G. Egeberg, P. Blom, K.G. Knudsen Top. Catal. 52, 229-240, 2009.

[6] D.U. Murzin, I. Kubickova, M. Snare, P. Maki-Arvela, J. Myllyoja, US Patent, 7491858B2, 2009.