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Research Article

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Production of Fuel Range Hydrocarbon Blended with Jet A-1 via Catalytic Hydrocracking Technique

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Abstract Preparation of upgraded palm biodiesel using heterogeneous catalyst (Zn Al_2 O_4) at batch and continuous processes is investigated.

The present study is an attempt to establish the possibility of use upgraded palm biodiesel as a blend component with jet A-1 at various volumetric ratios of (3, 10, 15 and 20 %) to prepare a new bio jet fuel specified physicochemical properties within the limits of jet A-1 standards. Regarding product from batch process at 300 ºC for 3 hours reaction time, the bio fuel with 3, 10 and 15 % upgraded ester content had almost similar characteristics with jet A-1 aviation. The physicochemical properties of binary blend (3 %) were: kinematic viscosity, density, high heating value and freezing point are 1.65 mm^2/s, 0.802 g/l, 46.56 MJ/Kg and -28 ºC respectively. GC/MS results indicate that the % composition of hydrocarbon range (C_8- C_{16}) in various binary blends are 97.3, 95.5, 92.4 & 90.48 % for binary blends (3, 10, 15 & 20 %) respectively while that of jet A-1 was 99.8%. While upgraded palm biodiesel produced from continuous process by hydro cracking procedure at 450 and 500 ºC in presence of hydrogen at 60 bars and 2 ml/L liquid hourly space velocity (LHSV) improved the freezing point of 3 % blend to -43 ºC without any additive and -52.5 ºC using 0.4 % of organic additive . Also % composition of hydrocarbon range (C_8- C_{16}) reached about 98 %.

Keywords Bio-Jet, Biodiesel, Hydrothermal catalytic cracking, upgraded palm biodiesel

1. Introduction

Due to the respect of environmental concerns, other energy sources replace diesel worldwide. Some of these renewable energies added to the world energy roadmap are the solar energy [1-2], the geothermal [3], the hydroelectricity [4], the wind power [5], the ethanol fuel [6], the biomass [7-8] and of course the bio- fuel [9].

Global consumption of jet fuel is about 190 million gallons /day [10]. This big volume of consumption illustrates the necessity of displacement even a small percentage with a renewable alternative fuel [11]. Also the goal of the International Air Transport Association (IATA) is the reduction of CO_2 emissions to 50 % by 2050 relative to 2005 levels [12].

Bio fuels have the potential to reduce CO_2 emissions fuel to the consumption of this gas during their sources growth [9, 13].

Fatty acid methylester (biodiesel) is more problematic as a bio – jet fuel at high flight altitude due to low temperatures encountered [14]. So; biodiesel needs additional processing such as upgrading [15], distillation [16] or precipitation of saturated ester using urea [17] to achieve low temperature requirements.

Aviation flights are exposed to low operating temperature so; jet fuels should not freeze in these environments. Pumping, Plugging of filters and related operating fuel problems are dependent on freezing point, for this reason, jet fuel specifications should include the value of minimum freezing point [18]. Freezing point of biojet fuel can be reduced by using hydrocarbon additives to meet required specific of ASTM D2386, they are often added only in measurable parts per million. Many authors investigated the effects of biodiesel on low freezing point temperature and different fuel properties [19-11].

The application of bio-fuels in transportation has been extended to the application as aviation fuel [21-24]. Aviation is a global industry with global problems and challenges that also demands global solutions. The International Air Transport Association (IATA) predicts commercial aviation to grow annually by 5% until 2030, exceeding expected fuel efficiency improvements by approximately 3%.

The main aim of this study is to produce fuel range hydrocarbon by upgraded palm biodiesel and to prepare various blends of bio jet fuel with typical Egyptian petroleum derivative (Jet A-1) and determine their characteristics to select the most suitable blends which may be used as new fuel blends which offers physicochemical properties within the limits of the conventional aviation fuel.

2. Methodology

2.1. Materials

- Biodiesel from palm oil feed stock to produce aviation bio-fuel.
- Upgraded biodiesel using Zn Al_2O_4 as catalyst [15].
- Jet A-1 was obtained from Egyptian ministry of civil aviation.

2.2. Experimental Technique

2.2.1. Bio-Jet fuel production

Experimental steps for Bio-Jet fuel preparation:

a. Biodiesel production:

Palm biodiesel obtained by transesterification of palm oil using KOH as catalyst (0.7% w/v) and methanol (2.5 % v/v) at 65ºC for 2 hours. The separated biodiesel is washed with 5% acetic acid solution in hot water to produce pure palm biodiesel.

b. Zn/Al_2O_4 catalyst preparation:

The gel precipitate was obtained by mixing solution of Zinc nitrate with aluminum nitrate (Co – precipitation method) [15].

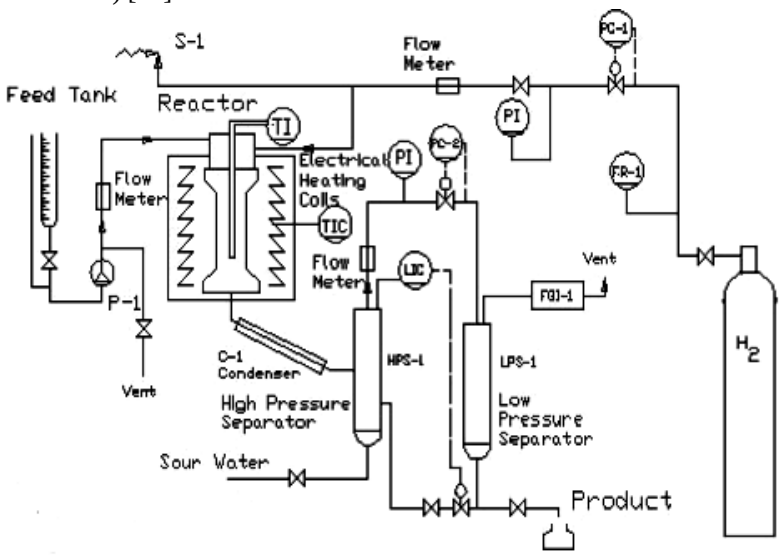

Figure 1: Schematic diagram of the Cata-test unit

2.2.2. Batch Upgrading process:

The upgrading of the biodiesel is achieved through two steps, described as following.-

2.2.2.1. Thermal Catalytic Hydro Cracking Process

This process is accomplished in a reactor under pressure (3.7 L) using Zn/Al_2O_4 as catalyst**.** The reactor vessel is charged with 360 ml palm (or other non-edible vegetable oil) biodiesel and catalyst (2.5 % w/v) at 300 ºC for 3 hr. reaction time at a mixing rate of 60 r.p.m.

After completing the reaction time; the reaction mixture is transferred to the second upgrading step.

2.2.2.2. Fractional distillation

Distillation of upgraded palm biodiesel resulting from the first upgrading process was carried at 250 ºC to evaporate the light fraction of palm biodiesel with improved properties.

2.2.3. Continuous Catalytic Hydro Cracking Process

This process is preceded in a tubular flow reactor shown in figure (1), known as Cata-test unit.

F Q-1: Flow quantity meter FR-1: flow recorder LIC: Level Indicator Controller

PC: Pressure Controller PI: Pressure Indicator P-1: Pump

TI: Temperature Indicator TIC: Temperature Indicator Controller

The hydrocracking of palm biodiesel has been carried out in a high pressure micro-reactor unit (Cata- test unit for cracking). The unit consists of a stainless steel reactor (internal diameter 19 mm, external diameter 27 mm, for cracking and length 50 cm).

It is divided mainly into three zones (a feed zone, a fixed-bed zone system and a product separation zone), each of them is heated and separately temperature controlled. Fifty ml of the catalyst is charged in the middle zone of the reactor.

The hydrocracking reaction has been carried out at different operating conditions of temperature, but at constant hydrogen pressure and liquid hourly space velocity.

The range of temperature was between 450 ºC and 500 ºC while hydrogen pressure was 60 bars. The liquid hourly space velocity, (LHSV), was 2 ml/hr. LHSV is defined as the ratio between the volumes of oil to the volume of catalyst as pumped to the reactor per hour. Palm biodiesel was pumped to the unit under pressure. The mixture was pre-heated before entering the fixed bed reactor where the feed molecules undergo hydro cracking reactions. The product exited in a mixed gas-liquid phase and was cooled before entering a high pressure-low temperature separator where the gas and liquid phases were separated.

2.2.4. Bio–Jet fuel blend preparation

2.2.4.1. Blend with upgraded biodiesel

Different fraction volumes (3, 10, 15 and 20%) of produced upgraded palm biodiesel were mixed with jet A-1 at room temperature. Analyses for these binary blended biojet fuels of their physical and chemical characteristics were performed.

2.3. Physicochemical Blend characterization

Various binary blending of jet A-1 with upgraded palm biodiesel were analyzed. The characterization included measurements of density, viscosity, high heating value (HHV) and gas chromatography mass spectra (GC/MS).

Density was measured using hydrometers at 20 ºC while for viscosity determination, Brookfield model DV-II+ viscometer was used at room temperature (27 ºC).

HHV was evaluated by determination the organic fraction (wt %) of C, H, N, S by microanalysis while O was calculated by difference.

HHV was calculated using modified Dulong formula [25] as follows:

HHV (KJ/Kg) = 4.18 * (78.4 * C + 241.3 * (H-O/8) + 22.1*S)

where C, H, O and S are in mass percent.

Freezing points for different blends were measured using Seta Freezing Point apparatus for aviation fuels within the range +5 to -65 ºC.

Gas chromatography Mass (GC/MS) was performed using a Thermo Scientific, ISQ Single Quadruple MS, TG-5 MS fused silica capillary column (30 m, 0.251 mm, 0.1 mm film thickness). For GC/MS detection, an electron ionization system with ionization energy of 70 EV (electron volt) was used. Helium gas was used as the carrier gas at a constant flow rate of 1mL/min. The injector and MS transfer line temperature was set at 280 °C. The oven temperature was programmed at an initial temperature 40 °C (hold 3 min.) to 280 °C as a final temperature at an increasing rate of 5 °C/min.

Also, total acid number (AV) for each ratio of binary mixture was calculated by dissolving weighted amount of sample in titrant solvent and titrated with alcoholic potassium hydroxide to a colorimetric end point.

3. Results and Discussion

3.1. Binary blends jet bio-fuel, from batch process, characterization

3.1.1. Physico-chemical properties and elemental analysis results

The upgraded palm biodiesel was mixed with jet A1 at various blending ratios (3, 10, 15, 20 % v/v). Binary blends were characterized chemically and physically to find the most suitable blending mixture which can be used in jet engine. All measured densities, viscosities, acid value, organic fractions (C, H, N, S, and O) and heating values are presented in Table (1).

A little variation in the density of binary blends refers to the variation in fraction of esters content in the mixtures of jet fuel according to the specifications and standard limits of Petron as, Malaysia, the density of jet A-1 must be in the range 0.775-0.84 g/cm^3 [26]. Results in Table (1) indicated that the densities of the binary blends are in the acceptable range for aviation purpose. All viscosity data reported in Table (1) were measured at temperature of 27 ˚C. The viscosities of binary of jet A-1 with upgraded palm methyl ester increases linearly with increase in the volume fraction of esters in the mixture. The results in Table (1) indicated that esters contents of 5 % and less have viscosities within the standard limits of aviation fuel.

Another property which characterizes the jet fuel is the acidity of the fuel expressed as acid value to ensure that the fuel does not contain any corrosive materials. The highest acid value means the lowest the quality only the blend less than 5 % is within the range.

Table 1: Values of physicochemical properties of binary jet fuel A-1 blends with upgraded palm biodiesel at various ratios

Properties	**Upgraded palm biodiesel**	**Various blend ratios**				**Jet A1 (kerosene)**
		3%	**10%**	**15%**	**20%**	
Density (at 20ºC- g/ml)	0.864	0.802	0.817	0.82	0.822	0.775-0.84
Kinematic viscosity (at 25ºC- mm^2/s)	4.23	1.6	1.7	1.72	1.74	1.599*
Freezing Point ºC	17	-25	-11	-6	-3	-47
HHV (MJ/kg)**	42	46	45.9	45	42	46.2
Acid value (mgKOH/g)	1.3	0.1	0.12	0.3	0.7	0.1
H/C ratio	3.58	3.0	3.1	3.17	3.29	< 1.91

***Kinematic viscosity (mm^2/s) at 25 ºC for jet fuel A-1 is according to the ASTM D341 method.**

The percent acidity can be controlled in the original produced biodiesel by limitation of feedstock, storage time and/or oil pretreatment. As can be seen in Table (1), the high heating value increases with decreasing the volume fraction of esters in the binary blends of jet A-1 with upgraded palm biodiesel but all the binary blends meet the minimum requirement of 42.8 MJ/Kg and fall within standard limit of jet A-1 [26].

Freezing points in Table (1) are still out the permissible range but it needs part per million additions of hydrocarbon additives to meet the required specifications of ASTMD 2386.

Hydrogen to Carbon H/C Molar ratio was 4,46 in Palm Oil, decreased to 3.58 in biodiesel and reached 3.59 for the light cut obtained after distillation of upgraded biodiesel. Noting that, increase of H/C molar ratio for binary blends indicated that, increasing the ratio of added bio fuel, replaced n- paraffin with cyclo-paraffin [27] which can affect the jet fuel combustion [28]. Higher H/C values in biojet obtained means that more drastic upgrading conditions are to be applied, *i.e.* thermal and hydrocracking may lead to better results.

3.1.2. G/C Mass analysis results

On the basis of the results GC/MS, aviation bio-fuels are generally produced from mixing traditional aviation Jet A-1 and hydrocarbons derived from upgraded palm biodiesel in which hydrocarbons selectivity is mainly between (C_8-C_{16}) fraction . According to (ASTM D7566 – 09 2009) aviation bio- fuel produced with binary blends of mixing proportion less than 50%. In this study the binary blends of 3 %, except the freezing point is still slightly higher, met the basic jet fuel mixing requirements.

For example, a broad percent paraffin composition of the binary blends 15 % is showed in Table (2). This wide variation in the composition, partially led to the formation of fuel better working groups.

Table 2: Fuel components of binary blends 15% in ideal carbon length C_8– C_{16} range hydrocarbon

n- paraffin	Iso-paraffin	Cyclo-paraffin	Aromatic
10.06 %	43.05 %	35.84 %	3.45 %

GC/Mass results demonstrate that: large number of the paraffin is alkanes with one or two attached methyl groups. Binary blends 15 % contains n – paraffin as "n–octane, n-decane and n-dodecane. A typical fuel about 43 % (iso–paraffin) contained mostly form C_{10} – C_{14} although iso-octane and iso cetane outside this range.

The aromatic fractions (≈3 %) in the binary blend 15 % are the alkyl benzene included (di-tri and tetra methyl) since tri- methyl benzene may be useful molecule in ignition limits [29].

Table (2) illustrates that major components in binary blends (15 %) are iso paraffin (43 %) and the results of GC/Mass analysis demonstrated that cyclo paraffin are rich in octane (di and tetra methyl) the role of cyclo paraffin in jet fuel combustion mechanism is not explained in previous literature [28] but little impact of cyclo paraffin in jet fuel combustion was noted in emissions [29].

Finally we can summarize GC/Mass results for the four binary blends in Table (3) as %C_8 – C_{16}.

Table 3: GC/Mass Results as C_8-C_{16} % range hydrocarbons

Binary blends	%C_8-C_{16}
Jet A1	99.2
3 %	97.3
10 %	95.5
15 %	92.4
20 %	90.48

3.2. Continuous Catalytic Hydrothermal cracking Experiment and blending of product with the jet fuel and determination of freezing point

Product cuts obtained by hydrocracking of palm oil biodiesel at different reaction temperatures 450 and 500 ^oC are blended with the Jet fuel A-1at 3 %v/v,

Freezing points results are presented in table (4). Pure cuts, freezing points decreased by increase of hydrocracking temperatures which reaches -13 ^oC.

The results of blending by 3 % of the obtained cut at 450 ^oC the freezing point reached -43 ^oC, which is improved more by adding the 0.4 % additive (2-Ethoxyethanol 99 %), as a freezing point depressing agent, to reach -47 ^oC .Using the cut obtained at 500 ^oC as 3 % blend added to it the 0.4 % additive gave the best result -52 ^oC freezing point as illustrated in table (4).

Table 4: Freezing points results by use of different blends and additives

Reaction Temperature ^oC	% Blending with Jet A-1	% Additive	Freezing Point ^oC
450	---	---	-5.5
450	3	---	-43
450	3	0. 4	-47
500	-	---	-13
500	3	0.4	-52.5

Results of GC/Mass of 3 % blend of bio jet produced from continuous catalytic hydro cracking process with jet A-1are illustrated in table (5).

Table 5: GC/Mass Results as C_8-C_{16} % range hydrocarbons of 3 % blend of biojet produced from continuous catalytic hydro cracking process

n- paraffin	Iso-paraffin	Cyclo-paraffin
17.3%	31.29%	49.41%

From the above table it is clear that cyclo paraffin content is higher than iso & n-paraffin which affect the combustion limits.

Conclusions

- In this study the 3 % binary blends ratio gave fairly good results concerning bio jet properties.

- The increase H/C molar ratio from elemental analysis indicated that some components of cyclo paraffin were replaced to n-paraffin.
- Preliminary experiments revealed that freezing point needs certain additives with different doses, for 3% binary blend of upgraded palm biodiesel with jet fuel A-1.
- It is obvious from the hydrothermal catalytic cracking treatment of the biodiesel at 500^{o}C is the optimum process to obtain the biojet blend, which when blended with Jet A-1 at 3% v/v, and organic additive at a ratio of 0.4 % , -52.5 ^{o}C is obtained.
- It is concluded that, temperature is the most significant factor affecting the freezing point of bio fuel.

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