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RESEARCH ARTICLE

PREPARATION AND EVALUATION OF CATALYTIC CRACKING PRODUCT OF NON-EDIBLE VEGETABLE OILS USING ACIDIC CATALYSTS

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ABSTRACT

Jatropha and Castor oils were obtained and transformed into their corresponding biodiesels by catalytic cracking using heterogeneous catalysts (Alumina and Montmorillonite-HCl) with different ratios (0.2%, 0.4%, 0.6%, 0.8% & 1%). The specifications of the obtained products were comparable to American Society for Testing and Materials (ASTM) specifications. The specifications of the obtained biodiesel were comparable to fuel properties of petroleum diesel. The suitable blend between the obtained biodiesel and fuel was described.

Key words: Catalytic Cracking; Biofuel; Castor oil; Jatropha oil.

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INTRODUCTION

Petroleum plays an important role in our life. Fuels, lubricants, sources of heat and power generation, and raw materials in the petrochemical industries are derived from petroleum. It is known that petroleum is a nonrenewable source of energy, and so it will disappear in one day of our future, so it is necessary to find other sources of energy in order to continue our life with ease. Scientists are now searching for new sources to replace petroleum. Biofuels are suggested to be the safest fuels to environment that can be used. In addition to having lower life cycle green house gas (GHG) emissions, sustainable biofuels should not compete with food or fresh water resources or contribute to deforestation. Oil-based energy crops that can meet these sustainability criteria include jatropha and castor oil. The choice of jatropha seed oil is favorable as it is non-edible oil, so there will be no competition with food crops. The biodiesel is characterized by determining its physical and fuel properties including density, viscosity, iodine value, acid value, cloud point, pour point and volatility according to ASTM standards. Biodiesel is preferable than petroleum diesel due to several characteristics including: ease of transport, renewable, effective in combustion process, low aromatic and sulfur content, high cetane number (Balat, 2008), and biodegradable (Demirbas, 2009).

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Biodiesel has higher parameters compared to petroleum diesel including: viscosity, cloud point, pour point, nitrogen oxide emission, and engine wear; and lower parameters such as: energy content, engine speed, and engine compatibility (Demirbas, 2008). Regarding the safety point of view, biodiesel has safety profits than petroleum diesel, as it is lower combustible and higher flash point (Onukwuli *et al.*, 2017). These biodiesels can be mixed with petroleum diesel in any proportion or directly used in diesel engine without modification (Gunawan *et al.*, 2011). The high cost of biodiesel is the major barrier to its commercialization (Demirbas, 2009), and 80 % of the total cost of biodiesel production is the cost of the raw materials (Wang, 2011). Biofuels are obtained by cracking of different vegetable oils including: Alcea pallid oil (Aysu, 2015), woody oils (Xu, 2010), soybean oil (Yu, 2013), palm oil (Sang, 2003), cotton seeds oil (Li, 2009), Jatropha oil (Biswas, 2014), and waste cooking oils (Tang, 2007). Cracking of vegetable oils performed either thermally without using any type of catalyst (Da Mota, 2014), or by using alkaline catalysts (Babich, 2011), metal oxides (Yigezu, 2014), zeolite (Zhang 2009; Li, 2014; Doronin, 2020). Owing to economic reasons, the use of low cost raw material such as: Egyptian castor oil (ECO) planted in Upper Egypt in Al-Alaki valley and irrigated using industrial and pretreated wastewater, is being considered for biodiesel production. Castor oil is planted in Upper Egypt and is widely distributed in the southern and southwestern regions with a total area of about 2,000,000 ha, and the annual seeds production is above 250,700 tons (Christopher Brickell, 1996).

The yield of the castor oilseed is about 40-60 %. In addition, the castor trees are gaining importance due to its low maintenance and fewer crop husbandry management practices required (Christopher Brickell, 1996). This paper aimed to evaluate the biodiesel that is produced from catalytic cracking of Egyptian castor and jatropha oils using ASTM standards, and compare its fuel properties with petroleum diesel.

MATERIALS AND METHODS

Materials

Jatropha and Castor oils were extracted from Jatropha and Castor seeds via hydraulic pressing; Alumina & Montmorillonite-HCl catalysts were purchased from (Sigma-Aldrich, Germany).

Methods

Extraction of Jatropha and Castor oils: Dry Jatropha and Castor seeds (500 g) were crushed individually using a hydraulic press until the oil was extracted. The oil was centrifuged to remove any solid contaminants and water, and used without further purification or treatment.

Catalytic cracking of Jatropha and Castor oil into biodiesel: Catalytic cracking procedures were performed as follows: 150 mL of Jatropha and Castor oils were charged individually in 500 mL two necked flask and (Alumina and Montmorillonite-HCl) catalysts were added individually at different ratios of (0.2%, 0.4%, 0.6%, 0.8% & 1%) by weight relative to oil. The mixture was mixed and allowed to thermal agitation for 4 hrs at 250 ^{o}C. The reaction products were collected by a condenser and their volumes were determined.

The obtained biofuels from the two oils were settled in a separating funnel to separate the produced water and then centrifuged to remove any contaminated or dispersed water. The reaction was completed and the products were: 75% biofuel, 15% water, 3% solids, and the rest were vapors. There are several parameters which affect the conversion reaction of Jatropha and Castor oils into biodiesels including: the catalyst ratio (%), conversion time and temperature. These parameters were studied to attain the optimized conversion reaction conditions.

Oil characterization: The fatty acid composition of the obtained Jatropha and Castor oils was determined using GC-Chromatographic analysis using GC-7890A instrument equipped with DB-23 column, 60 mm x 0.25 mm, i.d. of 0.25 µm. The characteristic properties of Jatropha and Castor oils were determined including the following: iodine value, acid value, kinematic viscosity at 40°C, density, cloud point, pour point, oxidation stability and sulphur content.

Biofuel specification: The characteristic specifications of the obtained biofuels such as: kinematic viscosity at 40°C, cetane number, density, pour point, cloud point, flash point, carbon residue and ash content were also determined according to ASTM specifications (ASTM, 2020; ASTM, 2011; ASTM, 2012; ASTM, 2007; ASTM, 2011; ASTM, 2011; ASTM, 2011 ASTM, 2010; Negm *et al.*, 2016).The suitable blend between the obtained biodiesel and fuel was described.

RESULTS AND DISCUSSION

The characteristic properties of Jatropha and Castor oils: The fatty acid profiles and the properties of Jatropha and Castor oils were listed in Table 1.

Properties of the obtained biofuel: The physical properties of the obtained biofuel were determined and compared to ASTM limits specifications. The measured characteristics were: kinematic viscosity at 40°C, iodine value, density, cetane number, pour point, cloud point, ash content, carbon residue and flash point were listed in Table 2.

The suitable blend between the obtained biofuel and gas oil fuel: In this study, many blends were made between the prepared biofuel and gas oil fuel. The suitable blend between the obtained biofuel and gas oil fuel was (10% Biodiesel + 90% Gas Oil). The results of this biodiesel blend were in acceptable range compared to gas oil fuel according to the standard values of ASTM specifications***Tables3-6***. The flash point of the obtained biofuel decreases than ASTM specifications (less than 52 ^{o}C), when the blending ratio of the prepared biodiesel to petroleum diesel increases than 10%.

Kinematic Viscosity at 40 ^{o}C: Kinematic viscosity represents the flow characteristics and the tendency of fluids to deform with stress. Kinematic viscosity is expressed in centistokes (cSt). For gas oil, the kinematic viscosity at 40 ^{o}C should be between (1.6 cSt –7.0 cSt) in ASTM D-445 (24). The obtained kinematic viscosity values of the prepared biodiesel blends were within the range of ASTM (3.07 cSt – 3.13cSt).

Cetane Number: The cetane number (CN) defines as the ability of fuel to ignite quickly after being injected. Higher value of (CN) indicates better ignition quality of fuel. For gas oil, the cetane number should be (min. 40) in ASTM D-4737(ASTM, 2010).The obtained cetane number values of the prepared biodiesel blend were within the range of ASTM (49 – 51). The higher value of cetane number of the produced biodiesel from Jatropha and Castor oils represents its high ability towards ignition in engines after injection.

Density: The density of the fuel represents the weight of one gram of it. The density is an important factor during the fuel processing and ignition, because the fuel represents an extra weight on the vesicle. Consequently, higher density of fuel will consume larger amount of fuel during the automotive work. For gas oil, the density value was (0.8394 g/cm^3) according to ASTM D-4052 (ASTM, 2011). The obtained density values of the prepared biodiesel blends were within the range of (0.8462–0.8472 g/cm^3), which is comparably slightly higher than the density of gas oil.

Pour Point: The pour point of the fuel represents the temperature at which the fuel becomes solid before it and liquid after it. Pour point is important characteristic during the transportation of the fuel at elevated low temperatures. In cold climate countries of low temperatures, high pour point fuels freeze. The pour point measurement is a standard test which applied to measure the flow properties of biodiesel during operating in cold weathers (Knothe, 2005).For gas oil, the pour point should be (max. 15 ^{o}C) in ASTM D-97 (ASTM., 2011).The obtained pour point values of the prepared biodiesel blends were within the range of ASTM (-6^{o}C to -9 ^{o}C).

Table 1. The fatty acid profiles and properties of Jatropha and Castor oils

Property	Castor oil	Jatropha oil
Fatty acid composition (wt %):		
Palmitic acid (C16:0)	1.00	15.20
Palmitoleic acid (C16:1)	-----	0.70
Stearic acid (C18:0)	-----	6.80
Oleic acid (C18:1)	3.00	44.60
Linoleic acid (C18:2)	5.00	32.20
Linolenic acid (C18:3)	1.00	-----
Arachidic acid (C20:0)	-----	0.20
Ricinoleic acid (C18:1, OH)	89.00	-----
Acid value, (mg KOH/g)	3.0	3.80
Kinematic Viscosity @ 40 °C, (mm^2/s)	43.0	37.0
Density, (kg/m^3) at 15 °C	0.959	0.910
Cloud point, (°C)	8	8
Pour point, (°C)	3	3
Oxidation stability, (h)	5.5	2.56
Iodine value, gI_2/100 g oil	80.5	104.46
Sulphur content %	0	0

Table 2. The properties of the biofuel obtained from the studied Jatropha and Castor oils

Biofuel Property	Castor oil	Jatropha oil
Cetane number	54	55
Kinematic Viscosity @ 40°C, (mm^2/s)	3.64	3.66
Density, (g/cm^3) at 15 °C	0.864	0.859
Cloud point, (°C)	3	3
Pour point, (°C)	-9	-9
Flash point, (°C)	150	161
Iodine value, gI_2/100 g oil	82.5	105.5
Carbon residue %	0.07	0.08
Ash %	Nil	Nil

Table 3. Physical & Chemical Properties of Biofuel* B10 (10% Biodiesel + 90% Gas Oil)
***Biofuel: Jatropha Oil with Alumina Catalyst (0.2, 0.4, 0.6, 0.8, 1 % conc.)**

Property	Biofuel* B10 (10% Biodiesel + 90% Gas Oil)					Gas Oil	Specification Limits	Test Method
	0.2%	0.4%	0.6%	0.8%	1%			
Density @ 15 ^{O}C gm/cm^3	0.8462	0.8463	0.8463	0.8468	0.8472	0.8394	Reported	ASTM D-4052
Flash point (P.M.C.C) ^{O}C	59	61	55	58	59	71	52 (min.)	ASTM D-93
Pour point ^{O}C	-6	-6	-9	-6	-6	-9	15 (max.)	ASTM D-97
Cloud point ^{O}C	3	3	3	3	3	3	-3 to 12	ASTM D-2500
Kinematic viscosity at 40 ^{O}C CSt	3.07	3.11	3.11	3.12	3.12	3.13	1.6-7	ASTM D-445
Recovery @ 350 ^{O}C ml	92	91	92	92	92	91	85 (min.)	ASTM D-86
Water and Sediment % vol	Nil	Nil	Nil	Nil	Nil	Nil	0.1 (max.)	ASTM D-2709
Total Sulphur % wt	0.036	0.038	0.037	0.036	0.040	0.047	1 (max.)	ASTM D-4294
Copper corrosion strip @50^{O}C/3hrs	1	1	1	1	1	1	1 (max.)	ASTM D-130
Carbon Residue %wt	0.08	0.06	0.07	0.08	0.06	0.07	0.1 (max.)	ASTM D-4530
Ash content % wt	Nil	Nil	Nil	Nil	Nil	Nil	0.01 (max.)	ASTM D-482
Color	2	2	2	2	2	2	4 (max.)	ASTM D-6045
Cetane index	51	50	50	51	51	49.3	40 (min.)	ASTM D-4737

Table 4. Physical & Chemical Properties of Biofuel* B10 (10% Biodiesel + 90% Gas Oil)
***Biofuel: Castor Oil with Alumina Catalyst (0.2, 0.4, 0.6, 0.8, 1 % conc.)**

Property	Biofuel* B10 (10% Biodiesel + 90% Gas Oil)					Gas Oil	Specification Limits	Test Method
	0.2%	0.4%	0.6%	0.8%	1%			
Density @ 15 ^{O}C gm/cm^3	0.8471	0.8471	0.8472	0.8471	0.8472	0.8394	Reported	ASTM D-4052
Flash point (P.M.C.C) ^{O}C	61	60	58	59	59	71	52 (min.)	ASTM D-93
Pour point ^{O}C	-9	-6	-6	-6	-9	-9	15 (max.)	ASTM D-97
Cloud point ^{O}C	3	3	3	3	3	3	-3 to 12	ASTM D-2500
Kinematic viscosity at 40 ^{O}C CSt	3.11	3.09	3.12	3.13	3.13	3.13	1.6-7	ASTM D-445
Recovery @ 350 ^{O}C ml	91	90	92	91	92	91	85 (min.)	ASTM D-86
Water and Sediment % vol	Nil	Nil	Nil	Nil	Nil	Nil	0.1 (max.)	ASTM D-2709
Total Sulphur % wt	0.040	0.041	0.039	0.038	0.041	0.047	1 (max.)	ASTM D-4294
Copper corrosion strip @50^{O}C/3hrs	1	1	1	1	1	1	1 (max.)	ASTM D-130
Carbon Residue %wt	0.07	0.06	0.06	0.08	0.08	0.07	0.1 (max.)	ASTM D-4530
Ash content % wt	Nil	Nil	Nil	Nil	Nil	Nil	0.01 (max.)	ASTM D-482
Color	2	2	2	2	2	2	4 (max.)	ASTM D-6045
Cetane index	49	50	51	50	51	49.3	40 (min.)	ASTM D-4737

Table 5. Physical & Chemical Properties of Biofuel* B10 (10% Biodiesel + 90% Gas Oil)
***Biofuel: Jatropha Oil with Montmorillonite-HCL Catalyst (0.2, 0.4, 0.6, 0.8, 1 % conc.)**

Property	Biofuel* B10 (10% Biodiesel + 90% Gas Oil)					Gas Oil	Specification Limits	Test Method
	0.2%	0.4%	0.6%	0.8%	1%			
Density @ 15 ^{O}C gm/cm^3	0.8466	0.8462	0.8465	0.8471	0.8472	0.8394	Reported	ASTM D-4052
Flash point (P.M.C.C) ^{O}C	60	61	62	59	60	71	52 (min.)	ASTM D-93
Pour point ^{O}C	-6	-9	-6	-6	-6	-9	15 (max.)	ASTM D-97
Cloud point ^{O}C	3	3	3	3	3	3	-3 to 12	ASTM D-2500
Kinematic viscosity at 40 ^{O}C CSt	3.10	3.13	3.11	3.13	3.12	3.13	1.6-7	ASTM D-445
Recovery @ 350 ^{O}C ml	90	9	92	90	90	91	85 (min.)	ASTM D-86
Water and Sediment % vol	Nil	Nil	Nil	Nil	Nil	Nil	0.1 (max.)	ASTM D-2709
Total Sulphur % wt	0.039	0.042	0.043	0.038	0.041	0.047	1 (max.)	ASTM D-4294
Copper corrosion strip @50^{O}C/3h	1	1	1	1	1	1	1 (max.)	ASTM D-130
Carbon Residue %wt	0.07	0.07	0.07	0.08	0.07	0.07	0.1 (max.)	ASTM D-4530
Ash content % wt	Nil	Nil	Nil	Nil	Nil	Nil	0.01 (max.)	ASTM D-482
Color	2	2	2	2	2	2	4 (max.)	ASTM D-6045
Cetane index	50	50	50	51	50	49.3	40 (min.)	ASTM D-4737

Table 6. Physical & Chemical Properties of Biofuel* B10 (10% Biodiesel + 90% Gas Oil)
***Biofuel: Castor Oil with Montmorillonite-HCL Catalyst (0.2, 0.4, 0.6, 0.8, 1 % conc.)**

Property	Biofuel* B10 (10% Biodiesel + 90% Gas Oil)					Gas Oil	Specification Limits	Test Method
	0.2%	0.4%	0.6%	0.8%	1%			
Density @ 15 ^{O}C gm/cm^3	0.8465	0.8464	0.8468	0.8468	0.8470	0.8394	Reported	ASTM D-4052
Flash point (P.M.C.C) ^{O}C	60	60	60	58	59	71	52 (min.)	ASTM D-93
Pour point ^{O}C	-9	-6	-6	-9	-6	-9	15 (max.)	ASTM D-97
Cloud point ^{O}C	3	3	3	3	3	3	-3 to 12	ASTM D-2500
Kinematic viscosity at 40 ^{O}C CSt	3.08	3.09	3.12	3.11	3.12	3.13	1.6-7	ASTM D-445
Recovery @ 350 ^{O}C ml	91	91	92	90	92	91	85 (min.)	ASTM D-86
Water and Sediment % vol	Nil	Nil	Nil	Nil	Nil	Nil	0.1 (max.)	ASTM D-2709
Total Sulphur % wt	0.038	0.038	0.038	0.036	0.039	0.047	1 (max.)	ASTM D-4294
Copper corrosion strip @50^{O}C/3hrs	1	1	1	1	1	1	1 (max.)	ASTM D-130
Carbon Residue %wt	0.07	0.06	0.08	0.08	0.07	0.07	0.1 (max.)	ASTM D-4530
Ash content % wt	Nil	Nil	Nil	Nil	Nil	Nil	0.01 (max.)	ASTM D-482
Color	2	2	2	2	2	2	4 (max.)	ASTM D-6045
Cetane index	49	49	50	50	51	49.3	40 (min.)	ASTM D-4737

Cloud Point: The cloud point is defined as the temperature at which a cloud of wax crystals first appears in a liquid when it is cooled. In general, wax crystals occur in two phases: nucleation and growth of crystals. The cloud point of biodiesel occurs during the start of wax cluster formation involving higher molecular weight components to give visible crystals (Moser, 2009; Knothe, 2005; Dunn, 2009). By continuous cooling of the sample, the agglomeration occurs. At this point, it involves the interaction between the high and low melting components to give bigger crystals. Low cloud points of the biofuels are important property due to the formation of regular clusters of the hydrocarbons lowers the fluidity of the biofuel which decreases its transportation through pipes and tubes. For gas oil, the cloud point should be (-3^{o}C to 12 ^{o}C) in ASTM D-2500 (26).The obtained cloud point values of the prepared biodiesel blends were within the range of ASTM (3^{o}C).

Flash Point: The flash point is the temperature at which the fuel becomes a mixture that will ignite when exposed to a spark or flame. Since biodiesel has high flash point, it is a safer fuel to transport and handle (Sandun, 2007). For gas oil, the flash point should be (min. 52^{o}C) in ASTM D-93.The obtained flash point values of the prepared biodiesel blends were within the range of ASTM (55 ^{o}C – 62 ^{o}C).

Carbon Residue: For gas oil, the carbon percentage should be (max. 0.1 %) in ASTM D-4530 (ASTM, 2011).The obtained carbon percentage values of the prepared biodiesel blends were within the range of ASTM (0.06 % – 0.08%), which are very low values and did not cause any potential on the environment when ignited.

Ash Content: For gas oil, the ash percentage should be (max. 0.01 %) in ASTM D-482 (ASTM, 2007).

The obtained ash percentage values of the prepared biodiesel blends were within the range of ASTM (Nil), which did not cause any potential on the environment when ignited.

Conclusion

From the results obtained in this study, the following conclusions can be recorded:

- Jatropha and Castor oils were converted into biofuel using heterogeneous catalysts (Alumina and Montmorillonite-HCl) with different ratios (0.2%, 0.4%, 0.6%, 0.8% & 1%).
- The specifications of the obtained products were comparable to ASTM specifications.
- The suitable blend between the obtained biofuel and gas oil fuel was (10% Biodiesel + 90% Gas Oil).
- The results of this biodiesel blend were in acceptable range compared to gas oil fuel according to the standard values of ASTM specifications.
- When the blending ratio of the prepared biodiesel to petroleum diesel increases than 10%, the flash point of the obtained biofuel decreases than ASTM specifications (less than 52 ^{o}C).

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