

Potential of Castor Oil as a Feedstock for the Production of Bio-fuel via Catalytic Hydro-Cracking

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ABSTRACT

The potential of castor oil; a non edible oil, as a feedstock for the production of a fuel that can be used as a substitute of regular petrol fuels has been assessed. The highly viscous castor oil was cracked into a blend of short chain hydrocarbons of much lower viscosity suitable for use as a fuel. The oil was hydro-cracked in presence of Co Mo/AL₂O₃ catalyst in a high pressure micro-reactor unit (cata- test unit for cracking). Since the composition of the product of the cracking process greatly depends on the process conditions, this research work has been done as to study the effect of the process conditions on the product yield as well as the product quality in terms of volatility, viscosity and freezing point. Hence, the conditions necessary for the production of a certain blend suitable for use as a fuel substitute of certain petrol fuel can be identified. The process conditions studied were the temperature, the pressure of hydrogen gas and the liquid hourly space velocity, LHSV. The process has been carried out at temperatures from 325 to 475 °C, a hydrogen pressure from 30 to 70 bar and at a liquid hourly space velocity, LHSV from 1 to 4 h⁻¹. The best yield of product which was about 87% was obtained by processing at 325 °C at a hydrogen pressure of 50 bar and LHSV 2 h⁻¹. The viscosity as well as the freezing point of the products obtained were measured and the results have shown that by cracking at low LHSV values (1-2 h⁻¹) at a temperatures of 425 or 475 °C yielded products of very low freezing point (-65°C to -70 °C) as well as very low viscosity suggesting the suitability of using those products as a bio-kerosene. However, the cracking at 425°C is preferred to that at 475 °C as the cracking oil yield was higher. Further studies are still recommended in this scope to adjust the process conditions to produce a bio-jet fuel using castor oil.

Key words: Castor oil, hydrocracking, biokerosene

Introduction

Currently, the fossil resources of fuel are not regarded as sustainable and questionable from the economic, ecology and environmental point of views (Bender, 2000). The burning of fossil fuels is a big contributor to increasing the level of CO₂ in the atmosphere which is directly associated with global warming observed in recent decades (Demirbas, 2006). The bio-fuels produced from the renewable resources could help to minimize the fossil fuel burning and CO₂ production. Bio-fuels produced from biomass such as plants or organic waste could help to reduce both the world's dependence on oil and CO₂ production. These bio-fuels have the potential to cut CO₂ emission and hence, reduce the problem of global warming (Kamm *et al.*, 2006; Naik *et al.*, 2010). This may be due to the fact that CO₂ released in burning plant biomass such as plant oils equals the CO₂ tied up by the plant during photosynthesis and thus does not increase the net CO₂ in the atmosphere. Additionally, bio-fuel production along with bio-products can provide new income and employment opportunities in rural areas. 21st Century is looking for a shift to alternate industrial feedstock and green processes to produce these chemicals from renewable biomass resources (Mabee, *et al.*, 2005).

Plant oils are considered a major feed stock for the production of bio-fuels to be used in diesel as well as turbine engines as substitute of petrol-fuels. However, the physical properties of plant oils especially their viscosities should be reduced to at least one third its value to guarantee efficient atomization in the engine and hence, efficient combustion. Such modification in physical properties can be achieved either by chemical or physical methods.

Among the chemical methods used are thermal decomposition of the oil in presence of a suitable catalyst, hydro-cracking of the oil under pressure and trans-esterification of oils with short chain alcohols. The latter method has been extensively used that yields a blend of fatty acids esters with alcohols known as biodiesel (Zaher, 1990; Zaher *et al.*, 2003; Demirbas, 2002; Quick and Woodmore, 1986; Zaher, 2001; Megahed, 1996; Zaher *et al.*, 2007; Zaher and El-Kinawy, 2012, Hawash *et al.*, 2009; Zaher *et al.*, 2004; Kusidiana and Saka, 2001; El-Kinawy and Zaher, 2012). Biodiesel has several advantages over regular diesel fuel. It is renewable and can be

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produced from many plant oils, free of sulfur which upon combustion produces corrosive acids, free of aromatics which contribute in particulate emissions. Also, it is a better lubricant to high pressure injection system parts which are sensitive to the fuel viscosity and it has a higher cetane number which enhances the auto ignition process. Moreover, it has a higher flash point which makes it safer and it has oxygen atoms in the molecules which improve combustion efficiency. Biodiesel is also environmentally friendly since it is biodegradable and eliminates lifecycle carbon dioxide emissions

The application of bio-fuels in transportation has been extended to the application as aviation fuel (Blakey *et al.*, 2011; Bogers, 2009; Hileman *et al.*, 2008; Gupta *et al.*, 2010). 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%. This implies that fuel consumption and emissions will continue to rise. The combination of increasing passengers demand and fuel costs and pressure to reduce anthropogenic emissions for which currently the sector accounts for 2-3% of the total global emissions, has pushed the aviation industry under considerable strain. Hence, the key objectives of commercial aviation are to find reliable fuel alternatives to cut costs and reduce volatility of fuel supply, climate effects, and improve fuel logistics. The relative rate of growth of the sector coupled with concerns around the environmental impact and the future security of supply of fuels has caused the sector to rapidly investigate the potential use of alternative fuels in aviation gas turbines. The use of bio-jet fuels in commercial aviation has received considerable attention in recent years, as it is currently seen as one of the best short to medium term option to answer the challenges on global scale. After a multi-year technical review from aircraft makers, engine manufacturers and oil companies, biofuels were approved for commercial use in July 2011 (http://en.wikipedia.org/wiki/Aviation_biofuel). Since then, some airlines have experimented with using of bio-fuels on commercial flights. In order to cope with the worldwide trends in partial replacement of currently used petro- fuels by bio-jet fuel, the aviation sector in Egypt is currently so concerned with starting of an industry for the production of bio-jet fuel in Egypt.

Most commonly used technologies are those involving plant oils as feed stock. Examples of plant oils used are jatropha oil, rapeseed oil, soybean oil and used cooking oil (Refaat *et al.*, 2006). It should be emphasized that the composition of the bio-fuel depends on the feed stock. The carbon-hydrogen-oxygen ratio, the number of carbon atoms in the molecule, the number of double bonds in bio-fuel can vary from one type of feed stock to another. Even, the variation in the molecular structure of bio-fuel can vary from one vegetable product to another. Such differences in the molecular structure of bio-fuel markedly affect the bio-fuel properties relevant to their efficient use in diesel or gas turbine engines and consequently, they will affect the performance of an engine running using these fuels.

Several technologies are available for bio-fuel production from plant oils including trans-esterification with short chain alcohols (Dizge *et al.*, 2009), thermal cracking and catalytic hydro-cracking (Bezergianni and Kalogianni, 2009). The last technology has a significant potential since the bio-fuel produced using this technology has better fuel properties and it also improves engine fuel economy

Industrial production of bio-fuel would be successful whenever the technology used is properly selected and when the feedstock to be used in this industry is available in quantities sufficient to guarantee a continuous and steady production process. In Egypt, there is a very wide gap between the consumption rate of edible oils and the local production rate of these oils. More than 90% of the oil needed for edible purposes is imported to cover this gap which represents a burden on the national economy. Therefore, it becomes not acceptable at all to establish an industry for the production of bio-fuel using vegetable oils that can be used for edible purposes. Castor beans which grows natively in Egypt since so many decades can provide the oil feedstock for the establishment of an industry to produce biofuel from a non edible oil and it can also be irrigated by semi-treated waste water.

This work has been initiated to assess the potential of castor oil as an oil feedstock for the production of bio-fuel using catalytic hydro-cracking technology.

Experimental

The hydrocracking of castor oil 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, 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. A schematic layout of this unit is shown in figure (1). The hydrocracking reactions of castor oil have been carried out at different operating conditions of temperature, hydrogen pressure and liquid hourly space velocity. The range of temperature was between 325 and 475°C while that of hydrogen pressure was 30 - 70 bar. The liquid hourly space velocity, (LHSV), ranged between 1 and 4 h⁻¹. LHSV is defined as the ratio between the volume of oil to the volume of catalyst as pumped to the reactor per hour. The castor oil was pumped to the unit with pressurized hydrogen (the ratio of hydrogen to oil was 350 L/L). The mixture was pre-heated before entering the fixed bed reactor where the feed molecules undergo hydrocracking reactions. The

product exited the reactor 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.

The liquid products were tested for their distillation characteristics, density, viscosity and freezing point following the ASTM standard test methods of petroleum products (American Society for Testing and Materials, 1995)

Specifications of the Catalyst

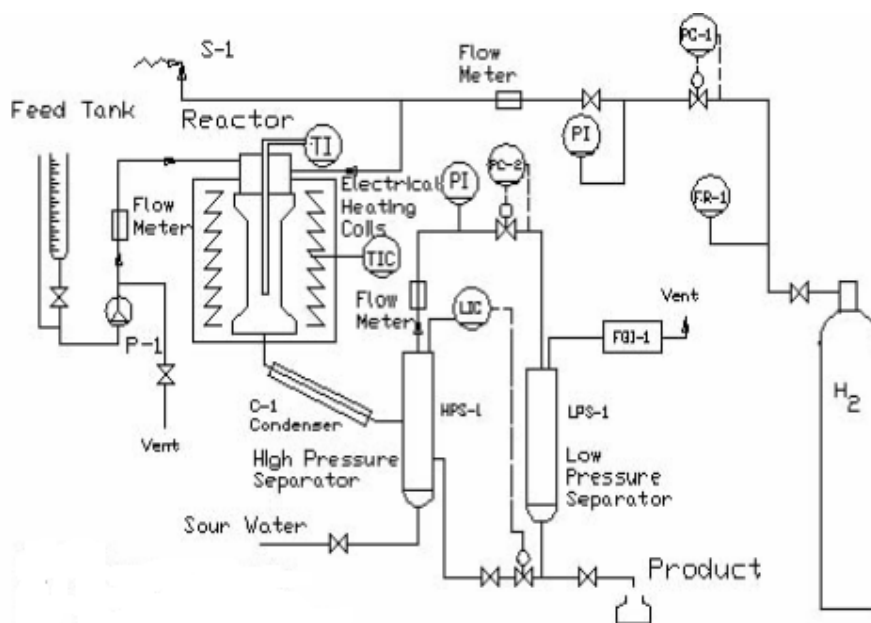
Fresh commercial catalyst CoMo/AL₂O₃ used as hydrocracking catalyst of castor oil was consisted of CoO=4 wt%, MoO₃=12 wt%, and AL₂O₃ balance (Table 1).

Table 1. CoMo/AL₂O₃ Specification

Characteristics	Fresh catalyst
Chemical compositions (wt%)	
Mo	12
Co	4
Al	84
Physical characteristics	
Surface area, m ² /g	165.48
Pore volume, cc/g	0.4591
Pore radius, A0	37.68

Characteristics of fresh catalyst.

The catalyst was pre-sulphided before the experiments with spiked light naphtha. Dimethyl disulphide (DMDS, 2 wt.%) was used as a spiking agent. The spiked light naphtha was passed through the catalyst bed with a flow rate of 1 ml/min under 15 bar hydrogen pressure and a reaction temperature 300°C for 12h.



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

Fig. 1: Schematic diagram of the cata-test unit

Results

The results of this work has been used to illustrate the effect of hydro-cracking conditions of castor oil on the product yield as well as the product characteristics.

Effect of cracking conditions on the product yield

The effect of cracking conditions on the product yield is shown in Tables (2-4) and Figs. 2-3. It is clear that the product yield decreased by increasing the cracking temperature. The yield decreased from 87% at 325°C to 75% if the cracking temperature was increased to 475°C (Table 2). According to the results listed in Table (3) and Fig.2, it seems that cracking castor oil using hydrogen at a pressure of 50 bar was optimum in view of the process yield which was 82% compared to 61% and 63% if the hydrogen pressure was decreased to 30 bar or increased to 70 bar, respectively. As shown in Table (4) and Fig.3, the increase in liquid hourly space velocity from 1 to 3h⁻¹ had very low or no effect on the process yield. However, further increase in this velocity to 4 h⁻¹ caused a pronounced decrease in the oil yield % from 80 to 71 %.

Table 2: Effect of Temperature on the product yield obtained by hydro-cracking of castor oil for three hours*

Temperature, °C	Input vol.,ml	Output liquid vol.,ml	Oil vol.,ml	Water vol., ml	Gases vol., ml	%Product yield
325	306	292	266	26	14	87
375	306	290	260	30	16	85
425	306	286	251	35	20	82
475	306	270	230	40	36	75

*At a hydrogen pressure of 50 bar and at a liquid hourly space velocity, LHSV=2h⁻¹, hydrogen to oil ratio 350 L/L by using CoMo/Al Catalyst.

Table 3: Effect of hydrogen pressure and input volume on product yield obtained by hydro-cracking of castor oil at 425°C *

Hydrogen pressure, bar	Input vol.,ml	Output liquid vol.,ml	Oil vol.,ml	Water vol., ml	Gases vol., ml	%Product yield
30	255	200	160	40	55	63
50	306	286	251	35	20	82
70	204	164	124	40	40	61

*Liquid hourly space velocity, LHSV=2h⁻¹, hydrogen to oil ratio 350 L/L using CoMo/Al Catalyst)

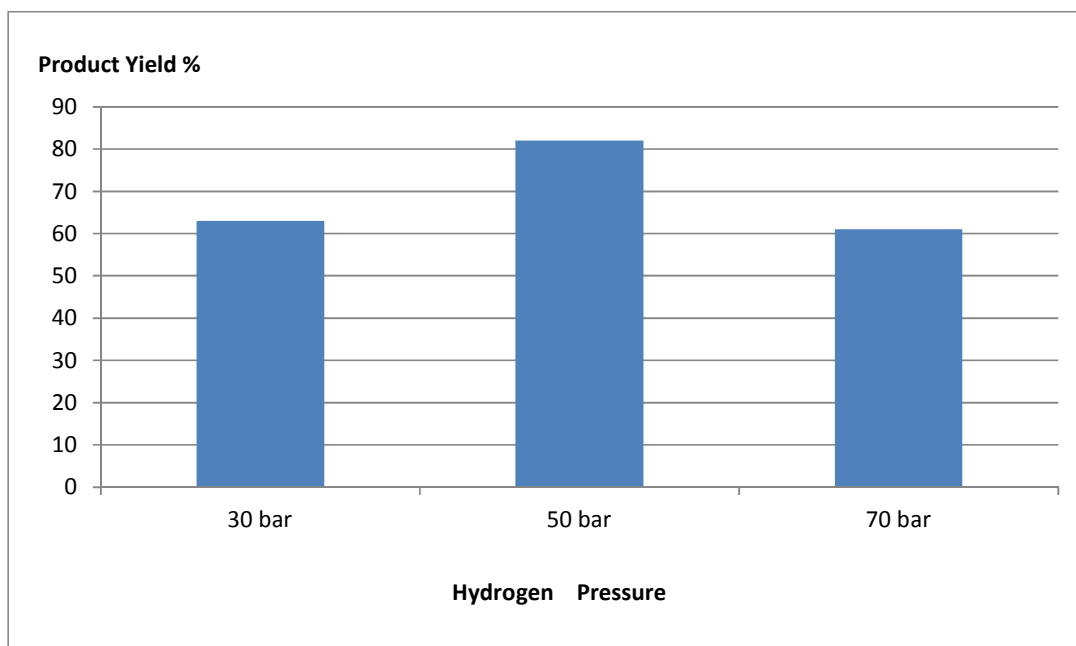


Fig. 2. Effect of hydrogen pressure on the product yield percentage obtained by hydro-cracking of castor oil at 425°C and LHSV= 2 hr⁻¹

Table 4: Effect of Liquid hourly space velocity (LHSV) and input volume on the product yield obtained by hydro-cracking of castor oil *

LHSV,hr-1	Input vol.,ml	Output liquid vol.,ml	Oil vol.,ml	Water vol., ml	Gases vol., ml	%oil yield
1	306	290	245	45	16	80
2	306	286	251	35	20	82
3	225	200	180	20	25	80
4	204	160	145	15	44	71

*At 425°C and hydrogen to oil ratio 350 L/L using CoMo/Al Catalyst

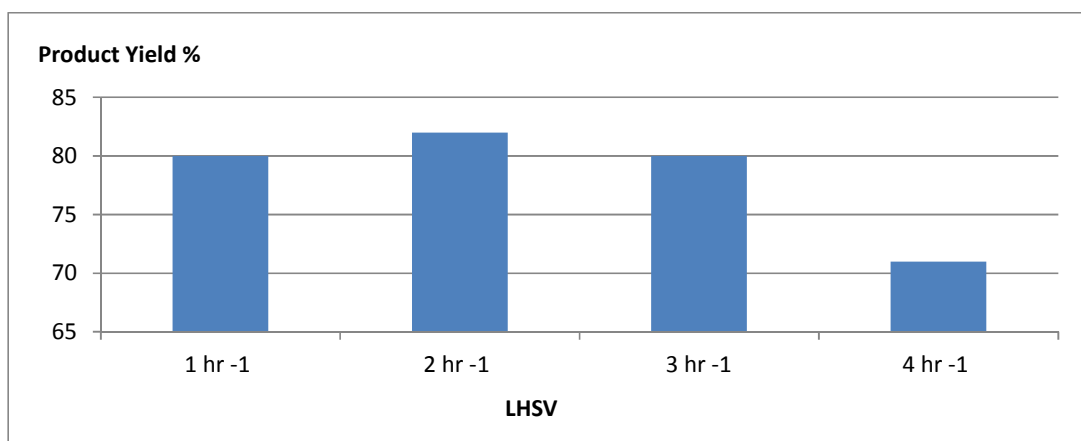


Fig. 3: Effect of Liquid hourly space velocity (LHSV) and input volume on the product yield percentage obtained by hydro-cracking of castor oil at 425°C

Effect of cracking conditions on the characteristics of the cracking products.

Effect of cracking conditions on the volatility of the cracking products.

The ASTM distillation results of the products obtained by cracking castor oil at different temperatures using hydrogen at a pressure of 50 bar and when the hourly liquid space velocity LHSV was adjusted to be 2 h⁻¹ are listed in Table (5). It can be stated that the cracking of castor oil at a temperature from 375°C to 425°C yielded products having a boiling range similar to that of gasoline (35-180°C). However, by increasing the cracking temperature to 475°C the obtained product had a boiling range in between those of gasoline and kerosene (35-250). The effect of LHSV on the volatility of the cracking product is clear in Table (6). The product volatility gradually decreased by increasing LHSV. However, the hydrogen pressure is less effective on the product volatility as shown in Table (7).

Effect of cracking conditions on the density, viscosity and freezing points of cracking products.

According to the results previously discussed, it seems that the products of cracking castor oil are more or less suitable as bio-kerosene rather than as biodiesel. One of the most important parameters for using a kerosene fraction as a bio-fuel especially in aircrafts is the freezing point which should not be higher than -47°C. It is clear from the results listed in Tables 8 and 9 that the cracking at 425 °C or 475°C will yield products of a very low freezing point that agree with the standard specifications of kerosene, provided that LHSV does not exceed 2 h⁻¹. The freezing point of the product of castor oil cracking at 475 °C was -71°C while that cracked at 425°C was -67 °C. These results may suggest the possibility of using these cracked products as a bio-fuel substitute of petrol kerosene. Cracking at 425°C is preferable than that at 475°C as the product yield was found to be greater at 425°C compared to that when the cracking was carried out at 475°C.

Table 5: ASTM distillation of products of cracking castor oil at different temperatures (hydrogen pressure, 50 bar, LHSV, 2h⁻¹)

ml recovered	Temperature		
	Oil Cracked at 375°C	oil Cracked at 425°C	oil Cracked at 475°C
Initial boiling point	36	36	50
10	40	46	88
20	56	58	98
30	78	66	110
40	80	74	129
50	100	96	148
60	116	110	174
70	130	130	206
80	130	130	240
90			310
Recovery	81	91	91
Residue	17	7	7
Loss	2	2	2

Table 6: ASTM distillation results of products of cracking castor oil at different LHSV (hydrogen pressure, 50 bar, Temperature 400°C)

ml recovered	Temperature		
	Cracked at LHSV 1h ⁻¹	Cracked at LHSV 3h ⁻¹	Cracked at LHSV 4h ⁻¹
Initial boiling point	50	86	75
10	80	102	100
20	100	118	136
30	120	140	164
40	140	188	198
60	220	280	284
70	240	300	298
80	280	330	314
90	310		320
Recovery	91	81	92
Residue	6	17	6
Loss	3	2	2

Table 7: ASTM distillation of products of cracking castor oil at different hydrogen pressure (Temperature 400°C, LHS, 2 h⁻¹)

ml recovered	Temperature	
	Cracked at Hydrogen press., 30 bar	Cracked at Hydrogen press., 70 bar
Initial boiling point	70	86
10	100	102
20	102	113
30	173	142
40	192	190
50	210	201
60	260	240
70	296	294
80	314	299
90	324	302
Recovery	92	91
Residue	6	6
Loss	2	3

Table 8: The effect of temperature on the density, viscosity and freezing point of castor oil hydro-cracked using hydrogen at 50 bar and LHSV, 2 h⁻¹*

Temperature, °C	Density, gm/cm ³	Viscosity, Cst	Freezing point, °C
325	0.8642	3.32	-28
375	0.7433	1.3	-38
425	0.7643	1.43	-67
475	0.7484	1.32	-71

*Hydrogen to oil ratio 350 L/L using CoMo/Al Catalyst.

Table 9: The effect of Liquid hourly space velocity (LHSV) on the density, viscosity and freezing point of castor oil hydro-cracked at 425 °C*

LHSV, h ⁻¹	Density, gm/cm ³	Viscosity, Cst	Freezing point, °C
1	0.7652	1.46	-65
2	0.7643	1.43	-67
3	0.7481	4.3	-23
4	0.8101	4.86	-18

*At hydrogen pressure of 50 bar, hydrogen to oil ratio 350 L/L using CoMo/Al Catalyst.

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