



Synthesis of Biodiesel by Pyrolysis of Castor Oil

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In this study, pyrolysis route was selected to produce the biodiesel from commercial grade castor oil. Three temperatures, 250, 300 and 350 °C were chosen with variable residence time from 10-30 min. All the reactions were carried out in the presence of hydrogen gas varying the initial pressure from 5-20 kg/cm². The fuel properties of the biodiesel like calorific value, cetane index, viscosity, cloud point, pour point *etc.*, were determined and it was found that the properties are very much closed to petroleum diesel. The maximum yield of 76 % was obtained in the present study. However, considering the fuel properties it has been observed that 350 °C reaction temperature, 20 min residence time and 15-20 kg/cm² initial hydrogen pressure can be the most suitable condition for the production of biodiesel from the castor oil.

Key Words: Castor oil, Pyrolysis, Biodiesel, Calorific value, Cetane index.

INTRODUCTION

Demand of energy has grown up by many folds over the last few decades. Majority of the world's energy needs are supplied through petrochemical sources, coal and natural gas. However, these conventional sources are finite and depleting very fast throughout the world¹. The rising prices of petroleum fuels, depletion of oil reserves and pollution problems related to fossil fuels are the driving forces behind the extensive search for renewable sources. An alternative fuel must be economically competitive, technically feasible, environmentally acceptable and readily available. In this search, biodiesel particularly those derived from vegetable oil showed a huge potential to supplement conventional fuel oil. Biodiesel seems to be an attractive source of energy because of its certain advantages over conventional fuels. (i) biodiesel is a renewable source and its supply is more or less assured in the future. (ii) its physico-chemical properties are comparable with the conventional fuel, petroleum diesel. (iii) all the organic carbon are of photosynthetic in origin, it does not contribute to raise the level of carbon dioxide gas in the atmosphere and consequently reduce the green house effect. Further because of its negligible sulphur content, it has low emission profile as compared to petroleum diesel in terms of SO_x formation. (iv) it is bio degradable. (v) considering the rising prices of petroleum fuels, its economic potential is also high in the future. (vi) it plays important role in the development of socio economic condition of the farmers²⁻⁶.

Almost 100 years ago Rudolph Diesel directly used vegetable oil as a fuel for his engine¹. Injection of vegetable oil directly in engine causes some problems because of its high viscosity, low volatility and higher concentration of unsaturated components compared to conventional diesel. Since then, continuous search is going on to find suitable route to convert the raw vegetable oil in to a diesel like material, *i.e.*, biodiesel. As such, there are three major routes to convert vegetable oil in to biodiesel: (i) chemical (ii) pyrolysis, *i.e.*, thermo chemical and (iii) biochemical as illustrated in Fig. 1. A lot of research work has been carried out in the area of transesterification⁷⁻¹¹. Hydrocarbons were produced in China by the thermal cracking of Tung oil during Second World War^{12,13}. Since then, number of studies have been carried out with different vegetable oils following the pyrolysis route with or without presence of catalyst. However, it has been observed, physico-chemical properties of the certain fraction of pyrolyzed oil are more or less comparable with the petroleum diesel¹⁴.

In India, the raw materials used for biodiesel production are non-edible oils obtained from various plant species such as Jatropha (*Jatropha curcas*), Karanja (*Pongamia pinnata*), Polanga (*Calophyllum inophyllum*), Castor (*Ricinus communis* L.) because of high cost of edible oil. Among these plants species castor oil plant (*Ricinus communis* L.), a drought resistant tree belongs to the *Euphorbiaceae* family. This plant can be found in all the tropical and subtropical countries of the world. It can be easily developed in uncultivated land and

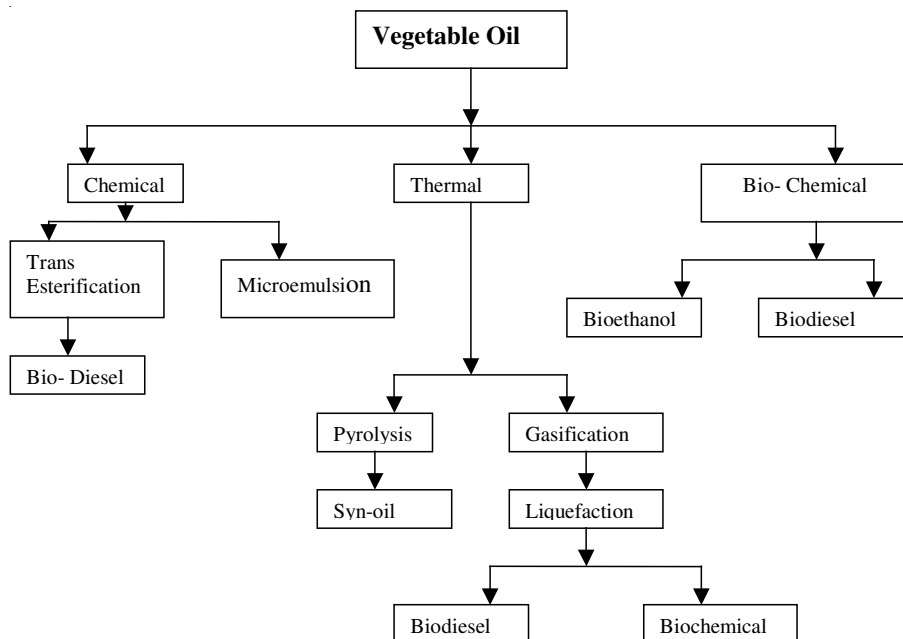


Fig. 1. Major routes to convert vegetable oil to biodiesel

wastelands in India. Castor oil is mainly composed of ricinoleic acid and some other acids. The fatty acid composition of some vegetable oils and that of castor oil are shown in Table-1¹⁵.

In India, very little research work has been carried out in biodiesel production from vegetable oil following thermo chemical processes. Considering the above facts, aim of the present study is to explore the possibility of conversion of castor oil to biodiesel through the pyrolysis route and fuel properties of castor biodiesel were also investigated.

EXPERIMENTAL

In the present study, commercial grade castor oil was selected as it is non-edible in nature and abundantly available in India. Basically, the castor oil is a triglyceride in which approximately 90 % of fatty acid chains are ricinoleic acid. Other important fatty acids are oleic acid and linoleic acid.

Pyrolysis study was conducted in a 4 L bolted closure autoclave having material of construction SS 316. The autoclave was having maximum allowable working pressure of 227 kg/cm² at 454 °C. The details of autoclave are shown in Fig. 2. Autoclave was fitted with variable speed magne drive stirrer (maximum operating speed 1500 rpm) having Dispersimax impeller for better gas-liquid contact. The stirrer was driven by microprocessor controlled magnetic drive. Autoclave was provided with the pressure gauge and safety devise like rupture disc and solenoid controlled emergency cooling system. It was also fitted with external heater having microprocessor based PID controller.

Measured quantity of castor oil was taken in the autoclave. Hydrogen gas of purity 99.9 % was introduced in to the autoclave to maintain the desired initial pressure. Initial hydrogen pressure was maintained within the range varying between 5-20 kg/cm² for all the experiments. Then, the temperature of the reaction mass was raised by external electrical heater assembly. Different experiments were carried out at the temperature ranging from 250-350 °C and residence time starting from 10-30 min

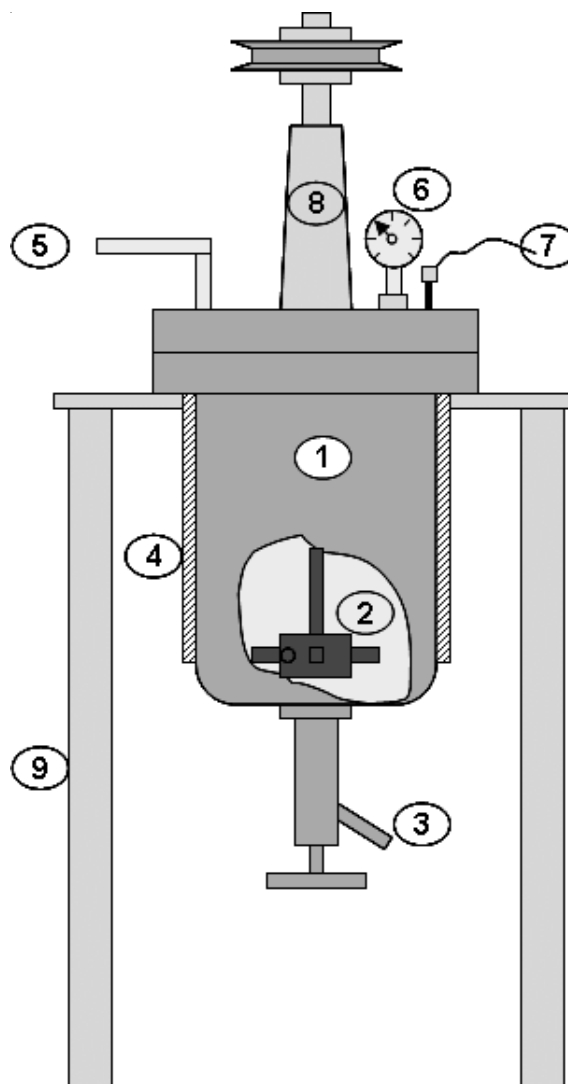


Fig. 2. Reactor system. (1) Autoclave, (2) Dispersimax stirrer, (3) Bottom drain valve, (4) Heating system, (5) H₂ Addition port, (6) Pressure gauge, (7) Thermocouple, (8) Magnetic drive, (9) Stand

TABLE-1
FATTY ACID COMPOSITION OF CASTOR OIL AND SOME VEGETABLE OILS

Fatty acid composition	Palmitic acid (C16:0)	Stearic acid (C18:0)	Oleic acid (C18:1)	Ricinoleic acid (C18:1) variety	Linoleic acid (C18:2)	Linolenic acid (C18:3)	Arachidic acid (C20:0)
Corn	11.67	1.85	25.16	0	60.60	0.48	0.24
Canola	3.49	0.85	64.40	0	22.30	8.23	0.00
Soybean oil	11.75	3.15	23.26	0	55.53	6.31	0.00
Sunflower oil	6.08	3.26	16.93	0	73.73	0.00	0.00
Castor oil	0.70	0.90	2.80	90.2	4.40	0.20	0.00

with the stirrer speed of 700 rpm. Desired reaction temperature was maintained by microprocessor based PID controller. After attaining the temperature, reaction mass was allowed to digest for residence time varying from 10-30 min. Finally, the product was collected from the bottom drain valve after cooling. The collected product was distilled (ASTM D-86 method) in the following fractions IBP-140 and 140-240 °C and greater than 240 °C. The heavier fraction *i.e.*, boiling range > 240 °C was taken and its characteristics such as calorific value, cetane index, kinematic viscosity, flash point, cloud point and pour point *etc.*, were determined.

RESULTS AND DISCUSSION

The main emphasis of this work was to check the diesel like properties of the converted oil. Therefore, calorific value, cetane index, flash point, pour point, cloud point, kinematic viscosity and yield of the products were determined. The effects of operating parameters on calorific value and cetane index have been discussed.

Calorific value: Reaction temperature, initial hydrogen pressure and residence time are most important factors which determine the quality of the product. In this study, calorific values of the products obtained at various temperatures and residence time were plotted against initial hydrogen pressure (Fig. 3).

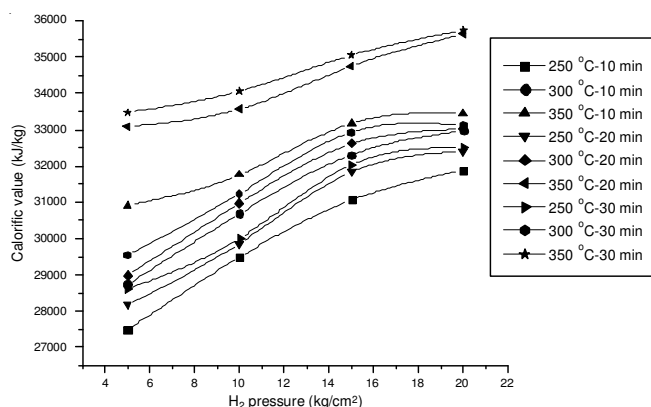


Fig. 3. Calorific value versus hydrogen pressure

Temperature: The influence of temperature on calorific value is clearly shown in Fig. 3. From Fig. 3, it can be seen that the product calorific value increases with the increase in temperature. However, when the temperature was raised from 250-300 °C, keeping other variables constant, the increment in the product calorific value was very small. On the other hand, when the temperature was raised beyond 300 °C, significant enhancement in the product calorific value was observed. The maximum product calorific value was obtained at 350 °C.

Residence time: From Fig. 3, it can be seen that influence of residence time on the product calorific value is very significant. It is observed that the product calorific value increases with the increase in residence time. However, the effect of residence time on the product calorific value at 350 °C is much higher, compared to that at lower temperature (250 and 300 °C).

Hydrogen pressure: From Fig. 3, it can be seen, the product calorific value increases with the increase in initial hydrogen pressure. However, the effect of hydrogen pressure on the product calorific value is more prominent at lower temperature. Considering the effect of above mentioned reaction parameters, it was found that significant change in calorific value did not occur at 350 °C with the increase in residence time from 20-30 min. Therefore, it is not meaningful to increase the residence time beyond 20 min.

Cetane index: Cetane index (CI) of the products obtained at various temperatures and residence time were plotted against initial hydrogen pressure (Fig. 4).

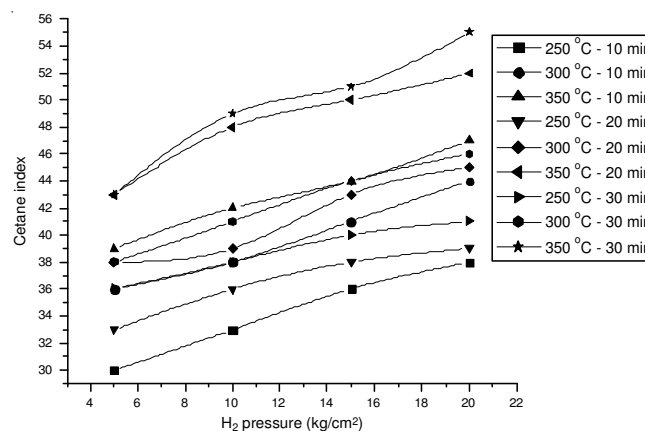


Fig. 4. Cetane index versus hydrogen pressure

Temperature: From Fig. 4, it is observed that the temperature plays major role for the enhancement of cetane index of the product. cetane index increases with increase in temperature. Maximum cetane index was obtained at 350 °C.

Residence time: Effect of residence time on the product cetane index can be clearly seen, from Fig. 4. Cetane index of the product increases with the increase in residence time. The influence of residence time on the product cetane index is more significant at 350 °C. At this temperature, when the residence time is raised from 10-20 min substantial improvement in cetane index of the product was observed. But, when residence time was increased from 20-30 min, increase in cetane index was not significant. But at the reaction temperatures 250 and 300 °C, the increase in product cetane index with the residence time is uniform.

Hydrogen pressure: From Fig. 4, it can be seen, cetane index of the product increases with the increase in initial hydrogen pressure. However, the rate of increase in the product cetane index is higher at higher temperature (350 °C) compared to the lower temperature zone, *i.e.*, at 250 and 300 °C.

It is justified to explain the reason for the increase in calorific value and cetane index with the reaction temperature and hydrogen pressure may be due to the hydrogenation of the products under the experimental conditions.

Other fuel properties of castor biodiesel: The physico-chemical properties petroleum diesel and castor biodiesel which is obtained at a reaction temperature of 350 °C, residence time 20 min and initial hydrogen pressure 20 kg/cm² are shown in Table-2. The flash point of castor biodiesel was found to be 170 °C as per ASTM method. This result was matched with in the ASTM limit (> 130 °C). The acid value of castor oil was determined as 5 mgKOH/g. The kinematic viscosity at 40 °C of castor biodiesel was found to be 8 mm²/s through pyrolysis route which is lower compared to the transesterification of castor oil¹⁵. The kinematic viscosity of the product is slight greater than the other biodiesel and petroleum diesel because castor oil is more viscous as compared to other feedstocks. Among all the fuel properties presented in Table-2, low temperature cold flow properties were determined in terms of cloud and pour point. The cloud point and pour point of castor biodiesel were found to be -20 and -40 °C, respectively. This result was better than the petroleum based diesel fuel. These cloud point and pour point of castor biodiesel are the most important fuel properties and that is very suitable for using in cold climate countries. These cold flow properties of biodiesel are measured by the types of fatty acid present in the vegetable oils. Higher the amount of unsaturated fatty acid present in vegetable oil better is the cold flow properties of biodiesel¹⁶. As castor oil contains more unsaturated fatty acid compared to other vegetable oils, the biodiesel obtained from castor oil is having better cold flow properties than other biodiesels. The other fuel properties were also determined as per ASTM methods and it was predicted that the fuel properties of castor biodiesel are very closed to the petroleum based diesel fuel.

Biodiesel fraction yield: In this study, yield of the biodiesel fraction *i.e.*, fraction having boiling range greater than 240 °C obtained at various reaction temperatures and residence time were plotted against initial hydrogen pressure as shown in Fig. 5. It can be seen from Fig. 5, with the increase in severity of the reaction *i.e.*, higher the temperature and

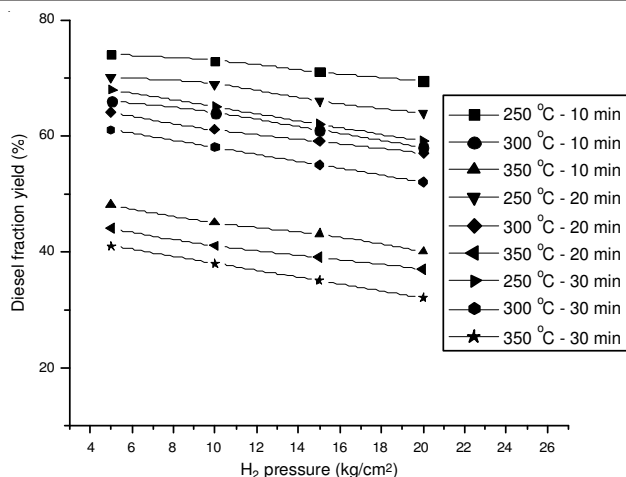


Fig. 5. Biodiesel fraction yield *versus* hydrogen pressure

pressure, the yield of the biodiesel fraction decreases. It was observed that maximum yield of 76 % biodiesel was obtained at lower temperature, *i.e.*, 250 °C with 10 min residence time at 5 kg/cm² hydrogen pressure. It can also be observed that when the temperature raised from 250-350 °C, the yield of biodiesel was decreased from 76-48 % at 10 min residence time and 5 kg/cm² hydrogen pressure. However, the lowest yield of biodiesel around 33 % was observed at 350 °C at 30 min residence time and 20 kg/cm² hydrogen pressure.

Conclusion

The results of this study clearly indicate that castor oil pyrolysis can generate a diesel like fraction under different reaction conditions. The physico-chemical properties such as calorific value, cetane index, viscosity, cloud point, pour point *etc.*, of the castor biodiesel have been studied and those are very much comparable to petroleum diesel. Other important observation is that the increase in initial hydrogen pressure for a fixed temperature and fixed residence time results in improved quality of the product. The yield of biodiesel fraction varied between a maximum of 76 % to a minimum of 33 % at different reaction conditions. In the present study it has been observed that higher the reaction temperature and pressure, better is the quality of the product but the yield of the biodiesel fraction decreases. Finally, considering the quality of biodiesel it may be concluded that the reaction temperature of 350 °C with residence time 20 min and initial hydrogen pressure of 15-20 kg/cm² is the most suitable condition for the production of biodiesel from the castor oil.

TABLE-2
PHYSICO-CHEMICAL PROPERTIES OF CASTOR BIODIESEL AND PETROLEUM DIESEL

Properties	ASTM test method	ASTM Limit	Petroleum diesel	Castor biodiesel
Kin. Viscosity@40 °C (cSt)	ASTM D 455	1.9-6.0	3.81	8
Flash point (°C)	ASTM D 93	> 130	68.3	170
Density@15 °C	ASTM D 1298	0.875-0.9	861.0	0.9279
Sulphur, (%) mass, max	ASTM D 5453	0.0015 %	0.20	0.0001
Cetane index	ASTM D 613	47	45	50
Water and sediments, % vol. max	ASTM D 2709	0.050	-	0.05
Cloud point (°C)	ASTM D 2500	-	2.0	-20
Pour point (°C)	ASTM D 6751	-	-6	-40
Cu corrosion	ASTM D 130	No 3, max	No. 1	No. 1

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