Role of Co-Solvent in the Super Critical Esterification process of Bio-Diesel Production through Karanja oil

Chandra Shekhar Singh¹, Naveen Kumar²

¹,²CASRAE, Delhi Technological University
rchandrashekhar85@gmail.com

Abstract. Biofuel is necessity for the today’s era for developing country like India to fulfil its growing energy demand and concern towards the environment pollution. Bio fuel production involve following major steps such as preparation of feed stock, selection of conversion technology and the up-gradation techniques. Conventional method of bio diesel production is of time consuming and sensitive to the feed stock quality. And due to these limitations in conventional esterification processes, Supercritical Esterification has now become one of the most attractive conversion technologies for bio diesel production due to its flexibility towards the feed stock quality, high conversion rate and fast reaction time. Although, it is costlier process as compare to the conventional processes because of its extreme condition of pressure and temperature requirement. So in the present study, the Super Critical Trans-esterification of Karanja (Pongamia Pinnata) oil with Methanol is investigated. And the effect of co-solvent on the reaction condition is studied. It has been observed from the results that use of co-solvent could be a potential means to reduce the critical condition required in the Super Critical Esterification process for the bio diesel production.

Keywords: Critical Point, Trans-esterification, Solvent

1. Introduction

Biofuel is necessity for the today’s era for developing country like India to fulfill its growing energy demand and concern towards the environment pollution. Biodiesel is one of the renewable sources to fill the gap. Biodiesel are known for their low PM (particulate matter) value, low emissions of CO and low Sulfur content[1]. Cetane number for biodiesel are also at higher side in compare to conventional diesel[2]. Vegetable oil like Mustard, Canola, Corn, Soybean, Palm and many more may be used to produce the Biodiesel but their cost and edibility makes them economically unviable. Second generation oil like Karanja(Pongamia Pinnata),Jatropha are now considered as the source for the biodiesel production[3]. Biofuel production involve following major steps such as preparation of feed stock, selection of conversion technology and the up-gradation.

Figure 1 Biodiesel Production Step

Bio diesel from vegetable oil can be converted by different methods like Pyrolysis, Dilution, Micro-emulsification and trans-esterification[4]. In trans-esterification process fat or oil react with alcohol
which results in form of esters and glycerides\cite{5}\cite{6}. In the process, a triglyceride molecule or fatty acid neutralize the free fatty acids removes the glycerin and creates an alcohol ester\cite{7}. Figure 2 is showing the actual reaction that takes place during the trans-esterification of vegetable oil.

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\begin{align*}
\text{H}_2\text{C-OCOR'} & \quad \text{Catalyst} & \quad \text{ROCOR}'+ \\
\text{HC-OCOR}'' & + 3 \text{ROH} & \quad \text{ROCOR}''+ \\
\text{H}_2\text{C-OCOR}'''' & \quad \text{mixture of alkyl esters (FAME)} & \quad \text{H}_2\text{O}
\end{align*}
\]

**triglyceride**  **alcohol**

**Figure 2 Trans-esterification reaction of vegetable oil\cite{8}**

In the trans-esterification reaction larger amount of alcohol is used to shift equilibrium towards the production of more alkyl esters. The reaction may be slow and need to be fastening to increase the yield. In that case catalyst is used to fast the reaction and yields. Trans-esterification process performed in the presence of base acid or enzyme catalyst \cite{6}. Selection of conversion technology depends upon the quality of feed stock such as acid value and water content\cite{9}.

In base catalytic trans-esterification, presence of water may cause saponification process that will lead the lower yields of esters. Separation of catalysts is also a problem. Although, Heterogeneous base catalyzed technology may reduce the cost of the catalyst separation. But this method also required to keep the water content in feed stock at very low level because of its sensitivity towards the water concentration\cite{8}. Acid catalyst may be an alternative to avoid the separation of the catalyst if the reaction is taking place homogeneously\cite{10}. Although, acid catalyzed reaction rate is low. Supercritical method is flexible towards the feed stock quality and free from the separation difficulty of catalysts\cite{5}. Saka and Kusdiana were reported the first time production of biodiesel under supercritical conditions. They were reported biodiesel production with 75-95% yield within 2 minutes at 350°C, 450 bar and M:O molar ratio of 42:1.

| Non-Edible oil     | Alcohol   | Oil to alcohol molar ratio | Temperature and Pressure | Time (min.) | Conversion rate(%) |
|--------------------|-----------|---------------------------|--------------------------|-------------|-------------------|
| Jatropha Curcas    | Methanol  | 01:40                     | 350°C, 200 bar           | 40          | > 90              |
| Cottonseedoil      | Ethanol   | 01:41                     | 250°C                    | 8           | 85                |
| Linseed oil        | Ethanol   | 01:41                     | 250°C                    | 8           | >85               |
| Sesame oil         | Ethanol   | 01:40                     | 325°C, 20 Mpa            | 40          | 100               |
| Pongamia Pinnata   | Ethanol   | 01:50                     | 400°C, 20 Mpa            | 30          | 90                |

Super critical esterification of vegetable oil is catalyst free weather it is homogeneous or heterogeneous\cite{11}. SAT (supercritical alcohol transestrification) may be defined as the process in which oil and alcohol(solvent) undergo above their critical point of pressure and temperature. Methanol and Ethanol are mostly used and proved alcohols for the super critical esterification.
process[12]. Super critical esterification process is very fast and yield is also very high in comparison of the conventional processes. In supercritical condition, the increase of reaction temperature resulted in higher yield irrespective of feed stock quality[13][14]. Additionally, in this method purification steps have also become easier as no catalysts are generally used. The trans-esterification reaction condition of different non-edible vegetable oils under supercritical condition tried by various researchers is shown in Table 1.

Despite of these advantages, Supercritical trans-esterification are costly as it requires high pressure and temperature which in turn increases the equipment cost and energy consumption[19]. The use of co-solvent could be a potential means to reduce the critical condition required in the Super Critical Trans-esterification process for the bio diesel production as well as lowering the cost of production. Co-solvent such as Carbon dioxide, propane, hexane and calcium oxide may be used to lower the extreme condition required[16]. So in the present study, the Super Critical Trans-esterification of Karanja (Pongamia Pinnata) oil with Methanol was investigated. And the effects of co-solvent on the reaction condition were studied.[13]

2. Supercritical Esterification of Karanja Oil for producing Biodiesel

Supercritical method of trans-esterification are required very extreme condition of temperature and pressure [20][21][22][23]. These extreme conditions makes the choice of equipment material very limited and so increases the initial cost of set-up. Despite of these, it has the advantages of being fast and tolerant towards the feed stock quality. It also facilitate the simultaneous trans-esterification and esterification of triglyceride and FFA respectively. Temperature and pressure as reported, affecting the distribution of biodiesel, glycerol, methanol and triglycerides. Kusdiana and Saka[24] were the first one to produce biodiesel through supercritical method and to explain the reaction mechanism in super critical condition. In supercritical method of trans-esterification process alcohol to oil ratio, temperature, pressure play very important role in the yielding of the biodiesel. It has been reported by researcher that in most of the supercritical methods of bio diesel production the reaction took place around 300°C to 400°C range of temperature and pressure range was around 200 bar[25][24]. Alcohol to oil ratio for various vegetable oil for optimum level was in the range of 40:1 to 42:1 [26][3][15]. Few reports also had shown that solubility of methanol was increased by 2%-3% on 10 °C increase of temperature[27]. But the above mentioned conditions are very severe and would cost very high in case of actual production. So, it is now a need to reduce the conditions required for the reaction and the use of co-solvent may be the one of the option to minimize the harsh condition required. Different types of co-solvents have been proposed such as carbon dioxide, propane, n-butane, n-heptane, n-hexane and many more has to be explored. It is reported that in biodiesel production through supercritical esterification with CO2 as co-solvent increases the yielding of methyl ester in case of canola oil bio diesel production[28]. A researcher is also reported that 0.1 molar ratio of propane reduced the extreme condition from 350 °C to 280 °C to obtain full conversion.

In the present paper, a lab scale supercritical trans-esterification of Karanja oil was conducted to determine the effect of co-solvent on the conditions required and yielding of bio diesel.

Method

The super critical trans-esterification was conducted in a tube of stainless steel[29]. The volume of steel vessel was 86 ml volume. The tubular reactor was made by stainless steel of grade SS 316 which is sufficiently hard and had strength enough to sustain the high temperature and pressure during the reaction. The schematic diagram of the experimental setup is given in figure 3. The experiment’s optimum condition was predefined for the Karanja oil with methanol in terms of molar ratio. During the experiment on set-up, when the reactor temperature reaches around the range of 300 to 400 °C then the pressure was noted around the 200 bar. The reactor was put into the heating bath to rise and maintained its temperature and time duration was recorded. Then reactor was cooled into the cold water bath to stop the further reactions. After 30 minutes for settle down, the fatty acid alkyl esters and glycerol were separated and analyzed.
The experiment was conducted in two phases, in first case non-catalytic supercritical esterification was conducted without any co-solvent and result was investigated. In the second phase the non-catalytic super critical trans-esterification reaction or experiment were conducted with CO\textsubscript{2} as co-solvent and the result were compared with the previous one.

![Experiment Setup](image)

for the study, locally purchased Karanja oil was used for supercritical esterification. The Methanol was fed in pure form and filled into the reactor vessel with the help of injection pump. Volume flow rate was calculated during the filling to maintain the methanol oil ratio. Important summary of reaction conditions are given in table 2.

Table 2 (Experimental Condition for experiment)

| Type of Condition          | Experimental Range      |
|----------------------------|-------------------------|
| Feed stock                 | Karanja Oil             |
| Reaction time              | 5- 30 min.              |
| Oil to alcohol molar ratio | 1: 41                   |
| Temperature                | 200-400 °C              |
| Pressure                   | 100-200 bar             |
2.2 Result and Discussion

The molar ratio of methanol, ethanol to oil plays very important role for the conversion of Esters. In the present study, when solvent was not used then for more than 90% conversion into methyl ester, the reaction temperature required was 350°C. The molar ratio was kept as 41:1 as suggested by various researchers for optimum yield. Due to high molar ratio, as temperature increases the pressure was also increasing in vessels. It was found that around 200 bars and within 12 minutes of time optimum yield in supercritical esterification was obtained. The conversion percentage with respect to the temperature when molar ratio was 41:1, can be observed in figure 4. For the conversion of 80%, the temperature required was 350 °C and the pressure was around 200 bars. From the above data, it is evident for more than 80% conversion a very severe condition is required which in turn increases the cost. While the introduction of CO2 as co-solvent was reducing the harsh condition required as compare to without it. Co-solvent was reducing the critical point of methanol oil mixture. Figure 5 shows that with CO2 as co-solvent, high yield of biodiesel can obtain at milder conditions.

As it can be observed from the figure 5 that with the use of the CO2 as co-solvent significant 67% yielding was obtained at the milder temperature around 200 °C as compare to the condition without co-solvent for the corresponding yield. More than 90 % conversion was found to be around the temperature 300 °C and conversion was also increased as compare to without Co-solvent.
From the figure 5 it can be seen that further increasing the temperature above 300°C there is no significant yielding in terms of conversion. After setting these parameters, again experiment was conducted with different molar ratio of CO2 to Methanol to investigate the effects on reaction. From the figure 6 it can be seen that when molar ratio is increased from 0.05 to 0.20, the conversion is starting from the 77% and obtaining conversion around 94% when the temperature reaches to the level of 350°C. From the figure, it can notice that temperature has positive effect on the yielding.

3. Conclusion
Present investigation is supporting the results of various researchers for the use of co-Solvent may be the one option to reduce the extreme conditions required. It can be observed from the results use of CO2 as co-solvent decreasing the extreme reaction conditions required and improving the reaction quality. Solubility of methanol in Karanja oil is increasing at low temperature with the use of co-solvent. Co-solvent is also decreasing the critical point of methanol so it resulting in milder condition required for the whole reaction process. Use of Co-solvent is enhancing the solubility between methanol and triglycerides at mild conditions and increases the biodiesel production. In the present study, a significant conversion around 70 to 80% had been found at mild conditions as compare to the super critical biodiesel production without the solvent use. It was also observed that by increasing the molar ratio of CO2 to methanol, have the positive effect on the conversion rate.

References:
[1] O. Farobie and Y. Matsumura, “State of the art of biodiesel production under supercritical conditions,” Prog. Energy Combust. Sci., vol. 63, pp. 173–203, 2017.
[2] Ö. Can, “Combustion characteristics, performance and exhaust emissions of a diesel engine fueled with a waste cooking oil biodiesel mixture,” Energy Convers. Manag., vol. 87, pp. 676–686, 2014.
[3] R. L. Patel and C. D. Sankhavara, “Biodiesel production from Karanja oil and its use in diesel engine: A review,” Renew. Sustain. Energy Rev., vol. 71, no. December, pp. 464–474, 2017.
[4] M. M. K. Bhuiya, M. G. Rasul, M. M. K. Khan, N. Ashwath, and A. K. Azad, “Prospects of 2nd generation biodiesel as a sustainable fuel - Part: 1 selection of feedstocks, oil extraction techniques and conversion technologies,” Renew. Sustain. Energy Rev., vol. 55, pp. 1109–
1128, 2016.

[5] V. I. Anikeev and E. Y. Yakovleva, “Biodiesel synthesis from vegetable oils with supercritical methanol,” J. Supercrit. Fluids, vol. 77, pp. 100–102, 2013.

[6] B. Singh, N. Kumar, and H. Muk, “A study on the performance and emission of a diesel engine fueled with Jatropha biodiesel oil and its blends,” Energy, vol. 37, no. 1, pp. 616–622, 2012.

[7] A. Demirbas, “Biodiesel production via non-catalytic SCF method and biodiesel fuel characteristics,” Energy Convers. Manag., vol. 47, no. 15–16, pp. 2271–2282, 2006.

[8] S. Semwal, A. K. Arora, R. P. Badoni, and D. K. Tuli, “Biodiesel production using heterogeneous catalysts,” Bioresour. Technol., vol. 102, no. 3, pp. 2151–2161, 2011.

[9] N. America, “Methyl Esterification of Free Fatty Acids of Rapeseed Oil as Treated in Supercritical Methanol,” vol. 34, no. 3, pp. 383–387, 2001.

[10] S. Bensaid, D. Hoang, P. Bellantoni, and G. Saracco, “Supercritical fluid technology in biodiesel production: Pilot plant design and operation,” Green Process. Synth., vol. 2, no. 5, pp. 397–406, 2013.

[11] A. Demirbas, “Biodiesel fuels from vegetable oils via catalytic and non-catalytic supercritical alcohol transesterifications and other methods: a survey,” J. Supercrit. Fluids, vol. 44, pp. 2093–2109, 2003.

[12] M. Balat and H. Balat, “Progress in biodiesel processing,” Appl. Energy, vol. 87, no. 6, pp. 1815–1835, 2010.

[13] A. Demirbas, “Biodiesel production from vegetable oils via catalytic and non-catalytic supercritical methanol transesterification methods,” Prog. Energy Combust. Sci., vol. 31, no. 5–6, pp. 466–487, 2005.

[14] A. Demirbas, “Comparison of transesterification methods for production of biodiesel from vegetable oils and fats,” J. Supercrit. Fluids, vol. 49, pp. 125–130, 2008.

[15] V. Rathore and G. Madras, “Synthesis of biodiesel from edible and non-edible oils in supercritical alcohols and enzymatic synthesis in supercritical carbon dioxide,” Fuel, vol. 86, no. 17–18, pp. 2650–2659, 2007.

[16] V. B. Borugadda and V. V Goud, “Biodiesel production from renewable feedstocks: Status and opportunities,” Renew. Sustain. Energy Rev., vol. 16, no. 7, pp. 4763–4784, 2012.

[17] A. Galia, O. Scialdone, and E. Tortorici, “Transesterification of rapeseed oil over acid resins promoted by supercritical carbon dioxide,” J. Supercrit. Fluids, vol. 56, no. 2, pp. 186–193, 2011.

[18] M. M. Gui, K. T. Lee, and S. Bhatia, “Supercritical ethanol technology for the production of biodiesel: Process optimization studies,” J. Supercrit. Fluids, vol. 49, no. 2, pp. 286–292, 2009.

[19] M. Y. Koh, T. Idaty, and M. Ghazi, “A review of biodiesel production from Jatropha curcas L. oil,” Renew. Sustain. Energy Rev., vol. 15, no. 5, pp. 2240–2251, 2011.

[20] M. Tobar and G. A. Núñez, “Supercritical transesterification of microalgae triglycerides for biodiesel production: Effect of alcohol type and co-solvent,” J. Supercrit. Fluids, vol. 137, no. November 2017, pp. 50–56, 2018.

[21] P. S. Montcho, C. Konfo T. R., P. Agbangnan D. C., A. Sidouhounde, and D. Sohounhloue C. K., “Comparative Study of Transesterification Processes for Biodiesel Production (A Review),” Elixir Appl. Chem., vol. 120, no. July, pp. 51235–51242, 2018.

[22] M. González Prieto, M. Fortunatti Montoya, P. E. Hegel, and S. Pereda, “Supercritical reactors for the production of advanced bio-fuels: A review,” J. Supercrit. Fluids, vol. 134, pp. 106–113, 2018.

[23] O. Aboelazayem, M. Gadalla, and B. Saha, “Biodiesel production from waste cooking oil via supercritical methanol: Optimisation and reactor simulation,” Renew. Energy, vol. 124, pp. 144–154, 2018.

[24] S. Saka and D. Kusdiana, “Biodiesel fuel from rapeseed oil as prepared in supercritical methanol,” vol. 80, pp. 225–231, 2001.

[25] D. Wen, H. Jiang, and K. Zhang, “Supercritical fluids technology for clean biofuel production,” Prog. Nat. Sci., vol. 19, no. 3, pp. 273–284, 2009.
[26] A. Abbaszaadeh, B. Ghobadian, M. R. Omidkhah, and G. Najafi, “Current biodiesel production technologies: A comparative review,” Energy Convers. Manag., vol. 63, pp. 138–148, 2012.

[27] M. N. Varma and G. Madras, “Synthesis of biodiesel from castor oil and linseed oil in supercritical fluids,” Ind. Eng. Chem. Res., vol. 46, no. 1, pp. 1–6, 2007.

[28] H. Imahara, E. Minami, S. Hari, and S. Saka, “Thermal stability of biodiesel in supercritical methanol,” vol. 87, pp. 1–6, 2008.

[29] K. T. Tan, M. M. Gui, K. T. Lee, and A. R. Mohamed, “An optimized study of methanol and ethanol in supercritical alcohol technology for biodiesel production,” J. Supercrit. Fluids, vol. 53, no. 1–3, pp. 82–87, 2010.