

Tetrahydrofuran-Assisted Transesterification Biodiesel from Waste Cooking Oil

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Abstract: Base-catalyzed transesterification of waste cooking oil for the production of biodiesel was assisted by the addition of cosolvent Tetrahydrofuran (THF). In addition to lowering of reaction temperature and reduction in reaction time for transesterification, THF facilitated production of methyl ester in a single phase. THF-assisted base-catalyzed reaction was optimized for various parameters. Maximum biodiesel production (92.8%) was obtained with 4% THF; 0.6% sodium methoxide (catalyst), 6:1 methanol to oil ratio, 45 min reaction time, 50^oC reaction temperature. Added to this, maximum glycerol recovery (18.62%) was obtained at 50^oC using lower concentrations of THF(2%). Use of THF highlights even more economically viable and greener potential for biodiesel production as this co-solvent is non-toxic, unreactive and of biomass origin.

Keywords: Biodiesel, waste cooking oil, transesterification, tetrahydrofuran, optimization

1. INTRODUCTION

There are some inherent problems associated with the use of basic catalysts in transesterification of oils and fats in biodiesel production [3]. These include additional inputs in terms of soap removal solvents, and energy inputs in terms of higher temperatures. Some of these steps may also not be environment-friendly. Although, use of heterogeneous catalysts may have some advantages [4-5], their disadvantages are also many, like high alcohol to oil molar ratio (12-30), high temperature (120-200^oC) and a very long reaction time of 3-8 hours [6]. Addition of co-solvents in the reaction medium is also an alternative approach which has been shown to enhance the reaction rates, as well as increasing the solubility and mass transfer between oil and methanol [7-8].

Tetrahydrofuran (THF) was chosen as a co-solvent as it possesses several advantages. THF has the ability to dissolve organic compounds at the hydrophobic side as well as bind water and alcohol on the hydrophilic side [9]. It is a non-hazardous and unreactive chemical with a low boiling point (67^oC). Further, THF is cheap and can also be co-distilled and recycled at the end of the reaction process.

Co-solvent transesterification of various edible and non-edible vegetable oils as well as animal fats has been investigated. Biodiesel production from Waste Cooking Oil (WCO) with this co-solvent has also attracted attention in the recent past as this feedstock has enormous potential in future [1]. THF-assisted biodiesel production has shown promising results with reference to improvement in transesterification efficiency [10-13].

There is a difference in the physicochemical properties of refined vegetable oils and the waste cooking oils. Moreover WCOs from different regions also differ in their viscosity, density and saponification values and free fatty acid composition [14]. Keeping this variation in mind, present investigations were carried out on waste cooking oil samples collected from restaurants in South Delhi, with an objective to ascertain optimal reaction conditions for THF-assisted methyl ester production.

2. MATERIAL AND METHODS

Waste cooking oil (WCO) was procured from the restaurants and eateries in South Delhi. The oil was subjected to experimental analysis for various physicochemical properties already outlined by Chauhan et al [1]. Since the free fatty acid content of this feedstock was < 0.2, no acid catalyst was required. The base-catalyzed transesterification reaction was carried out in a round-bottomed flask fitted with a magnetic stirrer. The reactor comprised pre-heated waste cooking oil, methanol, sodium methoxide catalyst and THF as a co-solvent. The process variables were optimized as a) Catalyst concentration, b) alcohol to oil molar ratio, c) THF concentration, d) Reaction time, e) Reaction temperature, and f) Glycerol recovery.

The Gas Chromatographic analysis of WCO-biodiesel was conducted to identify and quantify the FAME composition as per the already standardized protocol [2].

3. RESULTS AND DISCUSSION

The physico-chemical properties of waste-cooking oil were investigated by us earlier (Chauhan et al 2014). Due to its low free fatty acid value, this oil requires only one stage

catalytic process. The fatty acid methyl ester (FAME) constituted more than half (51.88%) by weight of the monounsaturated methyl ester, viz., oleic acid methyl ester (Methyl[12E] octadecenoate), making this fuel suitable for high temperatures[1]. In the present study, addition of THF

resulted in a slight reduction in the oleic acid methyl ester content (46.75%). Table 1 illustrates the fatty acid composition profile of biodiesel produced from present WCO samples.

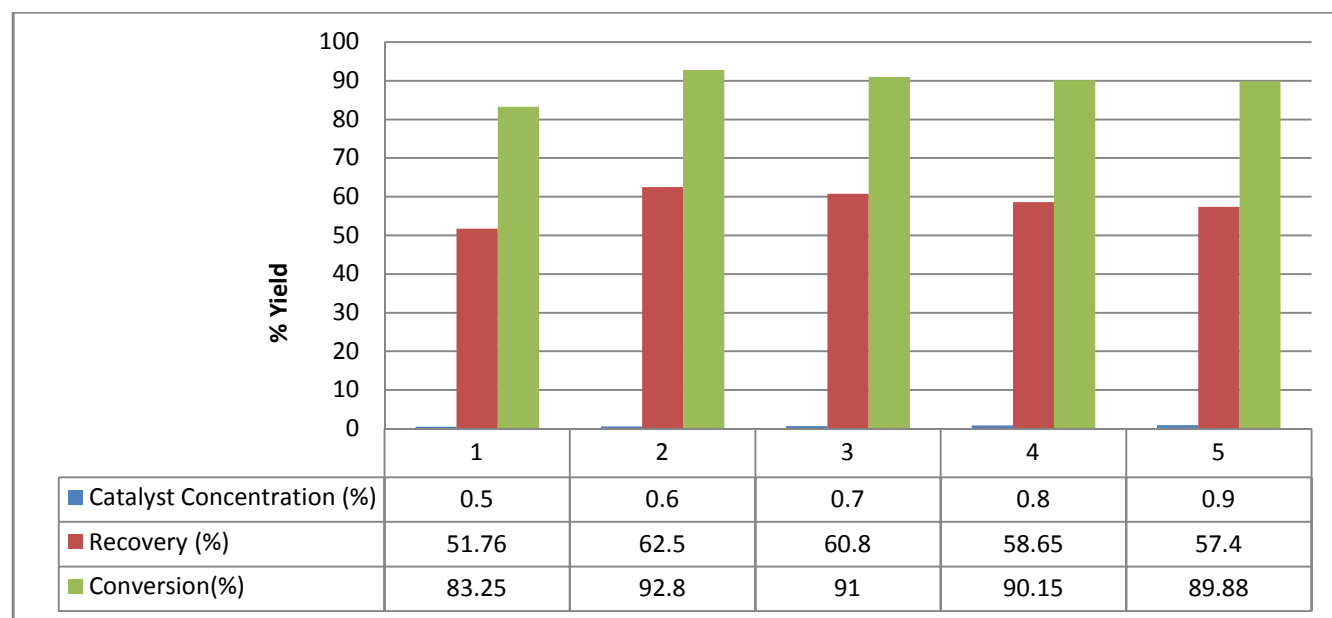
TABLE 1: Fatty acids composition of waste cooking oil biodiesel

FAME	Molecular Formula	Retention time	% peak area
Myristic Acid	C14:0	8.40	0.108
Palmitic Acid Methyl Ester	C17:0	12.34	13.318
Stearic Acid	C18:0	17.28	31.95
Oleic Acid	C18:1	18.57	46.750
Linolenic Acid	C18:2	19.36	6.423
Arachidic Acid	C20:0	20.39	0.393
Behinic Acid	C22:0	23.09	0.393
Overall total			98.703

3.1 EFFECT OF CATALYST CONCENTRATION ON BIODIESEL YIELD

The catalyst (sodium methoxide) concentration was varied from 0.5 to 0.9% (w/v of oil) keeping the other variables constant. Best catalytic concentration was found to be 0.6% where maximum recovery (62.5%) and conversion of oil to

methyl ester (92.8%) were recorded. Increasing the catalyst concentration resulted in a gradual decline in both conversion as well as recovery (Table 2). This decline could be attributed to an increase in viscosity and soap formation which causes difficulty in separation of biodiesel from glycerol [15].



THF to Oil Ratio-4%, Reaction Temperature-50⁰ C, Methanol to oil molar ratio-6:1

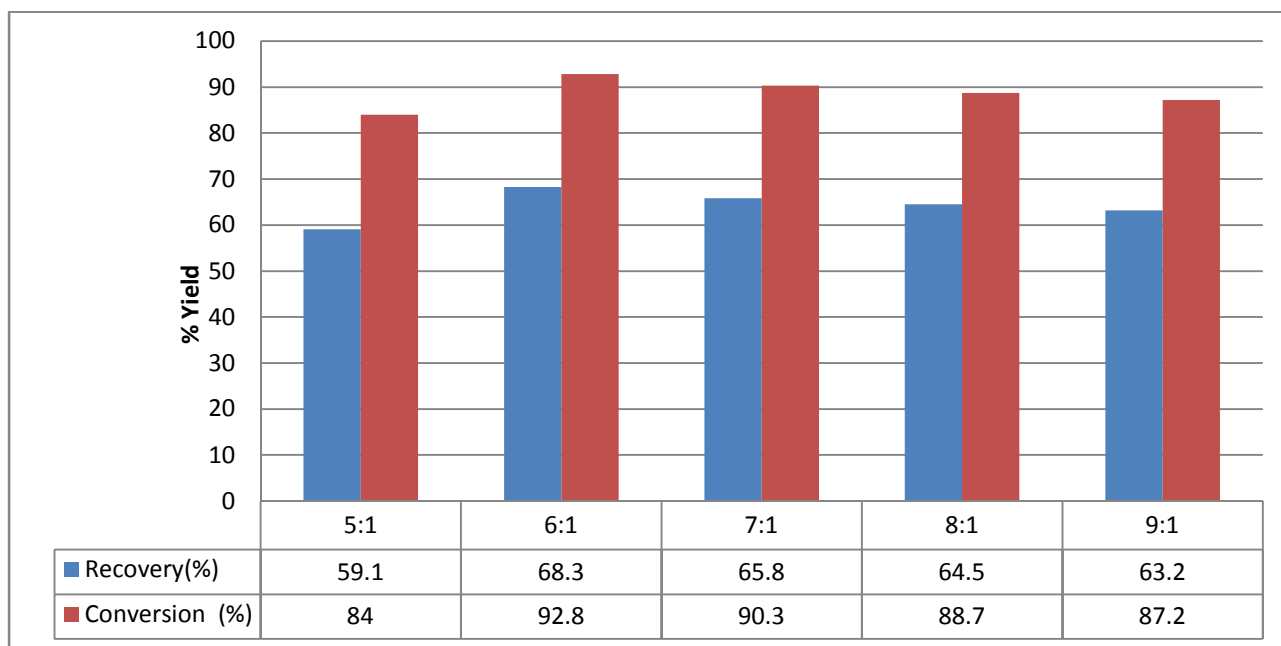
Fig. 1. Effect of catalyst concentration on biodiesel yield

3.2 EFFECT OF METHANOL TO OIL MOLAR RATIO

Effect of this important parameter was studied by using different methanol to oil molar ratios ranging between 5:1 and 9:1. Best results for recovery (68.3%) and conversion of WCO into its methyl ester (92.8%) were obtained at 6:1

methanol to oil molar ratio (Table 3). Values of both these sub-parameters declined as the methanol to oil ratio was increased beyond 6:1, which inhibited the catalyst active center. Since transesterification is an equilibrium-limited

reaction, the composition of the reaction mixture will decide the direction of the reaction.



THF to Oil Ratio-4%, Reaction Temperature-50⁰C, Catalyst concentration-0.6%

Fig. 2. Effect of methanol to oil molar ratio on biodiesel yield

3.3 EFFECT OF THF, REACTION TIME AND TEMPERATURE ON YIELD

Effect of THF concentration on biodiesel production at varying temperature revealed maximum yield at 50⁰C using 4% co-solvent (Table 4). Higher reaction temperature range was required (65⁰C) for a similar catalytic conversion without THF. Also, a much longer time period (3h) was needed to convert the waste oil stock feed to biodiesel [1].

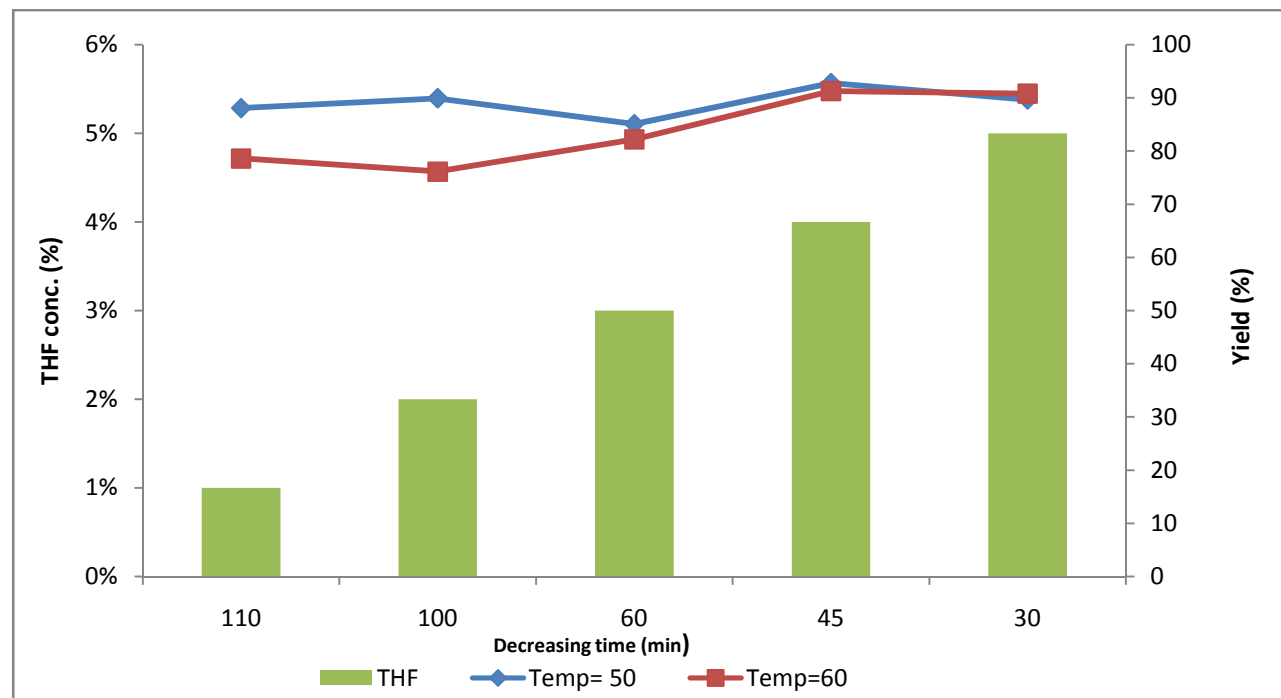


Fig. 3. Effect of THF concentration, reaction time and temperature on biodiesel yield

3.4 EFFECT OF THF AND TEMPERATURE ON GLYCEROL RECOVERY

Glycerol recovery (measured in terms of weight) at different temperature regimes was studied with respect to THF. Maximum recovery of glycerol (18.62%) was recorded at 50°C using 2% co-solvent. Increasing the concentration of THF to 4% and temperature to 60°C resulted in a decline in glycerol yield (Table 5).

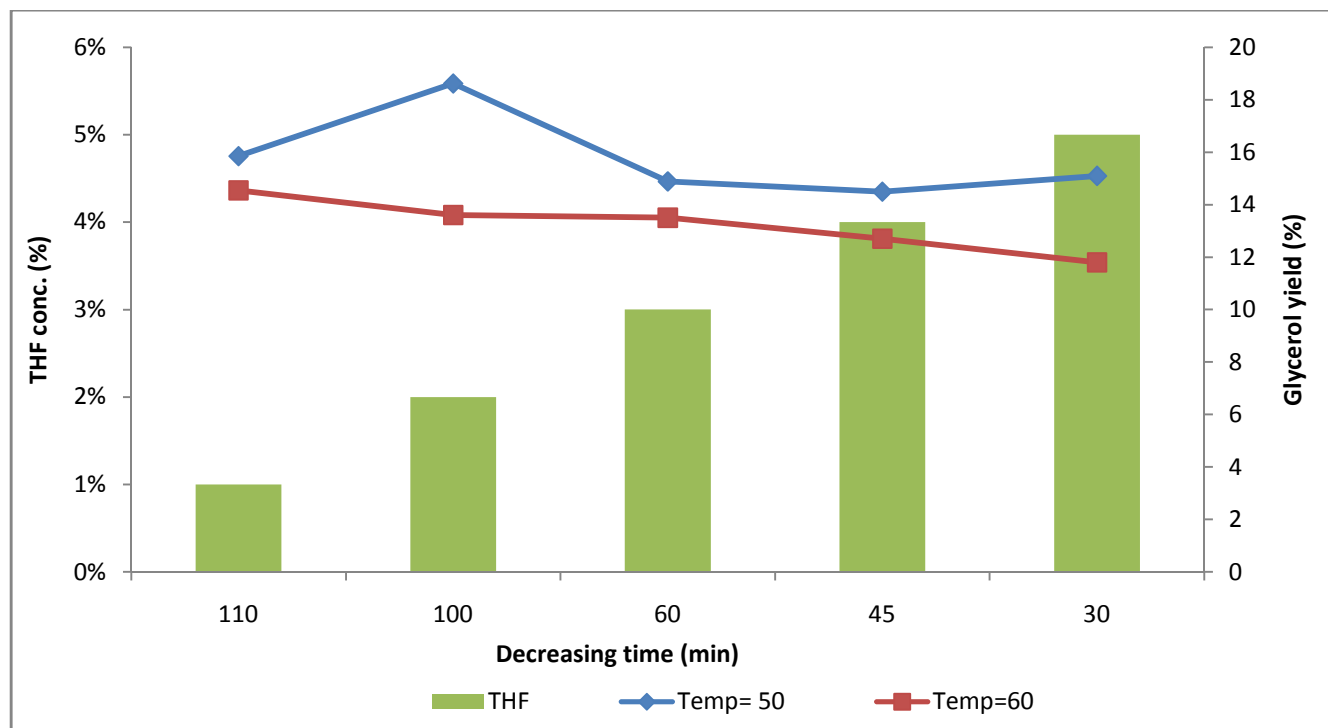


Fig. 4. Effect of THF concentration and temperature on glycerol recovery

4. CONCLUSIONS

These results indicate that THF accelerates the transesterification reaction and augments the conversion of triglycerides at lower temperature, requiring lesser concentration of catalyst. Similar results have been obtained in cottonseed oil [16], colza oil [17], rice bran oil [18] and chicken fat [19]. This makes THF as one of the most preferred green, clean and cheap adjunct for the biodiesel industry.

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REFERENCES

- [1] Chauhan, A.; Singh, V.K.; Verma, S.; Lahiri, S. Acid and base catalysed transesterification of used vegetable (gutter) oil and non-edible oils to fatty acid methyl esters. *Journal of Biofuels* 2014, 5(2), 68-75.
- [2] Chauhan, A. Fatty acid methyl ester (FAME) profile and characterization of biodiesel from waste cooking oil. *Napier Indian Advanced Research Journal of Science* 2015, 17, 31-34.
- [3] Meher, L.C.; Sagar, D.V.; Naik, S.N. Technical aspects of biodiesel production by transesterification—a review. *Renewable Sustainable Energy Reviews* 2006, 10, 248-268.
- [4] Helwani, Z.; Othman, M.R.; Aziz, N.; Fernando, W.J.N.; Kim, J. Technologies for production of biodiesel focusing on green catalytic techniques: A review. *Fuel Processing Technology* 2009, 90, 1502-1514.
- [5] Melero, J.A.; Iglesias, J.; Morales, G. Heterogeneous acid catalysts for biodiesel production: current status and future challenges. *Green Chemistry* 2009, 11, 1285-1308.
- [6] Jothiramalingam, R.; Wang, M.K. Review of recent development in solid, acid, base and enzyme catalysts (heterogeneous) for biodiesel production. *Indian Engineering Chemical Research* 2009, 48, 6162-6172.
- [7] Lam, M.K.; Lee, K.T. Accelerating transesterification reaction with biodiesel as co-solvent: A case study for solid sulfated tin oxide catalyst. *Fuel* 2012, 89, 3866-3870.

- [8] Boocock, D.G.B.; Konar, S.K.; Mao, V.; Sidi, H. Fast one-phase oil-rich processes for the preparation of vegetable oil methyl esters. *Biomass and Bioenergy* 1996, 11, 43-50.
- [9] Muyassaroh, E.D.D.; Hudha, M.I. Biodiesel dari Minyak Jarak Pagardengam Variasi Penambahan Co-solvent dan Waktu Reaksi. *Jurnal Teknik Kimia* 2012, 7, 8-11.
- [10] Lin, C.-C.; Hsiao, M.-C. Optimization of biodiesel production from waste vegetable oil assisted by co-solvent and microwave using a two-step process. *Journal of Sustainable Bioenergy Systems* 2013, 3, 1-6.
- [11] Zhang, Y.; Dube, M.A.; McLean, D.D.; Kates, M. Biodiesel production from waste cooking oil: 1. Process design and technological assessment. *Bioresource Technology* 2003, 89, 1-16.
- [12] Elkady, M.F.; Zaatout, A.; Balbaa, O. Production of biodiesel from waste vegetable oil via KM Micromixer. *Journal of Chemistry* 2015, 2015, 1-9.
- [13] Math, M.C.; Kumar, S.P.; Chetty, S.V. Technologies for biodiesel production from used cooking oil—a review. *Energy for Sustainable Development* 2010, 14, 339-245.
- [14] Pavalavana Pandian, J.; Prabu, B.; Pugazhivadivu, M. Indian waste frying oils: Influence of fatty acid composition on their physic-chemical properties. *Journal of Biofuels* 2014, 5(2), 83-95.
- [15] Encinar, J.M.; Gonzalez, J.F.; Pardal, A.; Martinez, G. Transesterification of rapeseed oil with methanol in the presence of various cosolvents, *Proceedings of Third International Symposium on Energy from Biomass and Waste, Venice, Italy. 8-11 Nov. 2010*, 1-17.
- [16] Jinsi, C.; Xiangyang, W.; Enzhu, H.; Yufu, X. Xianguo, H.; Lijun, P.; Shaotong, J. Biodiesel production by transesterification cottonseed oil with ethanol using tetrahydrofuran as cosolvent. *IEEE*, 2011.
- [17] Caglar, E. Biodiesel production using co-solvent. *European Congress of Chemical Engineering (ECCE-6) Copenhagen, 16-20 September, 2007 (Book of Abstracts)*.
- [18] Taggar, M.S.; Soni, R.; Singh, S.K.; i, S.S.; Sangha, M.K. Tetrahydrofuran-assisted base catalysed transesterification of rice bran oil for biodiesel production. *Journal of Biofuels*, 2014, 5, 62-67.
- [19] Fransiska, F.; Felicia; Si, Taslim, M. Biodiesel production from chicken fat using tetra furan as co-solvent. *Proceedings of the 5th Sriwijaya International Seminar on Energy and Environmental Science & Technology, Palembang, Indonesia. Sept. 10-11, 2014*, 27-31.