

# Enhancement of Co-Solvent Transesterification Using Reactive Distillation

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**Abstract** —The transesterification of waste cooking oil (WCO) is studied extensively. The efficiency and economical operation of bio fuel production depend on the ease of operation and cost control. Co-solvent hexane can reduce the time of reaction and enhance the recovery of an ester. Reaction, solvent recovery, and product separation are done in many steps. Reactive distillation offers an efficient and economical method of production of bio diesel. This research paper deals with optimizing reactive distillation parameters for co-solvent transesterification of WCO.

**Keywords:** *Reactive distillation, Transesterification, Co-solvent, Solvent recovery, Waste cooking oil and Bio diesel.*

## I. INTRODUCTION

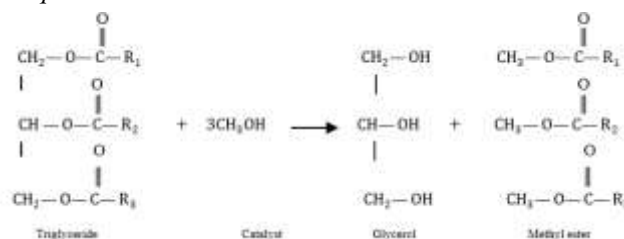
Depletion of fossil fuel and cost fluctuation of petroleum crude necessitates the search for alternate renewable products. Vegetable oils like palm, neem, groundnut, sunflower, rice bran, etc; after transesterification yields bio diesel with Cetane number requirements comparable to petroleum diesel. The costs of vegetable oils are high for they are used as cooking oil worldwide. The used cooking oil is available in large quantities at a cheaper price. If the waste cooking oil mixes in effluent stream, it gives corrosion initiation to metal piping and also makes effluent treatment costly. The transesterification process is used to convert the WCO to bio diesel. The conversion efficiency depends on the free fatty acid (FFA) present. If more than 2.5% FFA is present, acid treatment to neutralize the soap formation reaction with sodium hydroxide is introduced. Co-solvent n-hexane is used to make the reaction faster and easy separation of the product stream. The present research paper discusses the operating procedure and design parameters for high yields of bio diesel.

## II. PROCESS OF TRANSESTERIFICATION

Bio diesel can be produced by transesterification of triglycerides (TG) with alcohol (commonly methanol or ethanol) in the presence of a base or acid catalyst. The TG converted into step wise diglycerides (DG), monoglycerides (MG) and finally glycerol. The triglycerides (TG), when treated with catalyst and methanol, gives three parts methyl ester (Bio diesel) and one part of glycerol. In general, bio

diesel generated is equal to the volume of vegetable oil taken initially.

### A. Equations



Transesterification Reaction

### B. Free Fatty Acids (FFA)

In using waste cooking oil, the free fatty acid may pose a problem. FFA is present in the WCO due to oil breaking down while cooking.

### C. Problems of FFA

FFA reacts with sodium hydroxide to form soap and water. This gives problems in washing of ester-glycerin mixture. The catalyst requirement increases. The yield of ester is low.



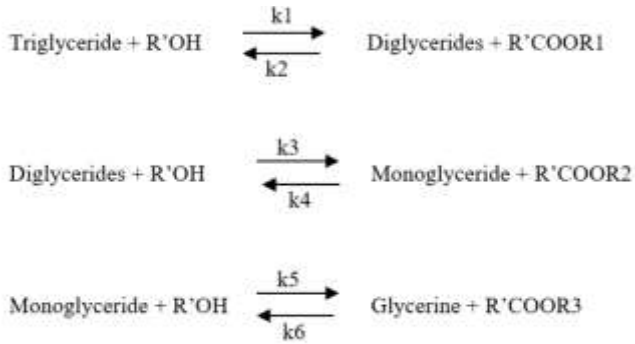
Formation of soap

### D. FFA above 2.5%

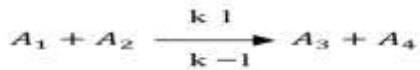
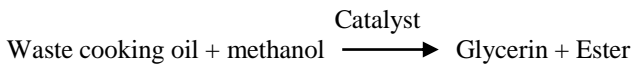
The waste cooking oil (WCO) containing more than 2.5% FFA is treated with required quantity of sulphuric acid. Transesterification using both types of WCO containing less than 2.5% FFA and more than 2.5% FFA is carried out. The glycerol is separated from the ester by siphoning system from the settling tank.

### III. REACTIVE DISTILLATION (RD)

The advantages of combining reaction and distillation in a single column are enhancement in reaction speed, increased conversion, avoidance of azeotropes, ease of product separation and uniform heat dissipation. The design of column dimensions and operating variables depends on the kinetics of the reaction and relative volatilities of the reactants and products. Options for homogeneous and heterogeneous catalysis are possible. One of the reactant may be recovered as top product and recycled back into the reactor. The bottom product is separated into heavy and light fractions in settling unit kept outside the column. The transesterification reaction may be expressed by the following kinetic steps;



#### A. Kinetic steps in transesterification



At equilibrium,

$$\frac{c_3}{c_1} * \frac{c_4}{c_2} = \frac{k_1}{k_{-1}} = k_c$$

The reaction velocity of reactant one can be described by

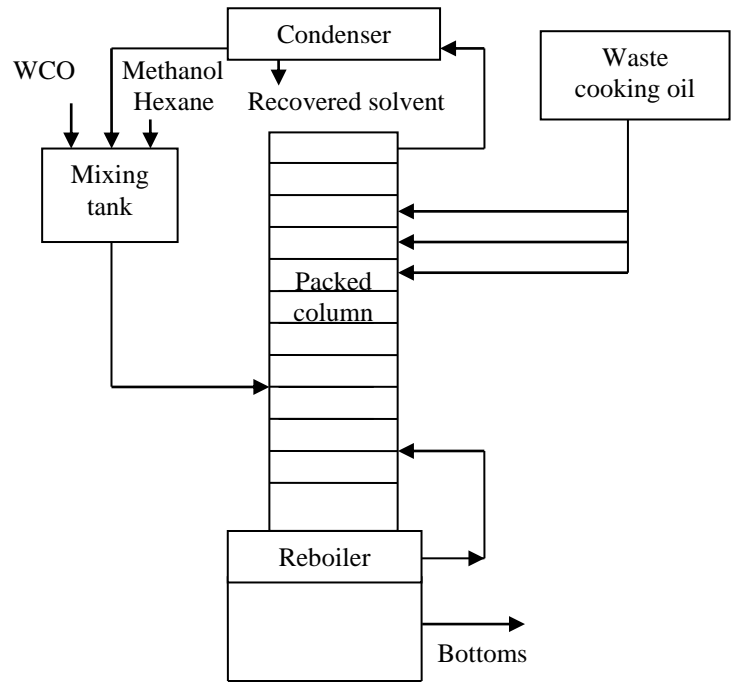
$$\tau = k_1 c_1 c_2 - k_{-1} c_3 c_4$$

The relative volatility of the reactant and products play an important role in designing the column. The residence time and rate constant influence the number of stages of reaction, fractionation and solvent recovery.

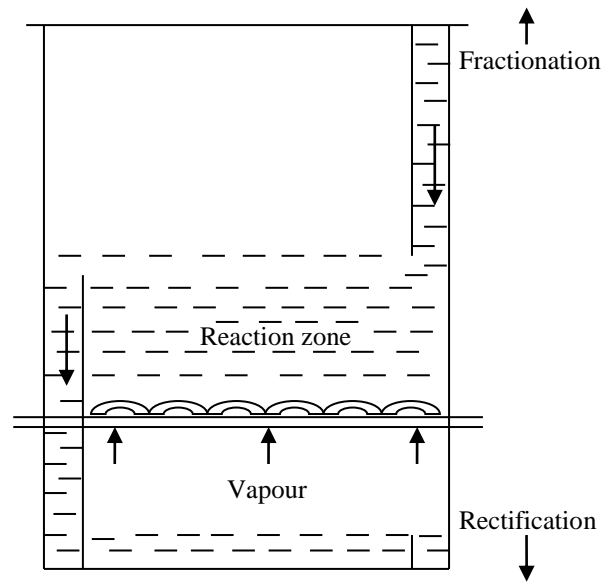
#### B. Equipment design for reactive distillation

Different types of equipments and operating procedures are followed depending on whether the reaction is slow or fast. The reaction, distillation, solvent separation takes place in a single column which reduces the plant cost and the operating expenses. The equipment may be plate column or a series of stirred vessels or cascade of stirred vessels. The co-solvent recovery is done in the fractionation stages above the reaction

zone. The numbers of stages for the reaction are decided by the kinetics and relative volatility of the system.



Flow diagram of Reactive Distillation



Reaction and Distillation Zones

#### C. Experimental setup

The experimental setup consists of glass column 30mm diameter and 600mm height packed with racing ring. The fractionating section consists of plates. A condenser is mounted at the top and attached with standard cone and socket

29/32. Thermo wells are provided to measure the temperature of the top and bottom of the column. Un reacted methanol is evaporated at the bottom using reboiler. The waste cooking oil is sent from the top using flow control device. Methanol and catalyst are mixed and heated separately. This mixture is fed to the reaction zone of the column using flow control device. Co-solvent n-hexane is used to improve the flow and reactivity of the waste cooking oil. The bubble caps mounted on the trays served as spargers. Weirs and down comer provided on the reaction zone helps to maintain liquid column through which the vapour bubbles and rises up creating agitation.



Experimental setup of reactive distillation

#### D. Materials and Methods

The methanol used is supplied by Changshu Hongsheng Fine Chemical Co., Ltd. The waste cooking oil is collected from the college canteen (Palm oil). NaOH is supplied by Rohini fine chemicals and n-hexane procured from S.D. fine chemicals.

#### E. Procedure

About 5 liters WCO is mixed with 1000 ml methanol and mixed in a separate vessel along with catalyst is heated to 50°C fed into the packed column. The waste cooking oil at 30°C is flowing at a residence time of 3 minutes. The reboiler is heated using heating mantle to a temperature of 100°C. The unused methanol/hexane is vaporized and moves up the packed column against the tickling down reaction mixture. The top column temperature is maintained at 62°C.

#### F. Result and Discussion

The final product obtained was a clear volatile liquid with the following characteristic properties.

TABLE I. PROPERTIES OF FINAL BIO DIESEL

APPEARANCE	VISUAL	CLEAR
SPECIFIC WEIGHT	USING SPECIFIC GRAVITY BOTTLE	0.85 KG / LITRE
BOLING POINT	RECORDED FROM EXPERIMENT	60°C
FLASH POINT	LAB SETUP	110°C
ODOUR	AROMATIC HYDROCARBON	
SOLUBILITY	INSOLUBIL IN WATER	
CETANE NUMBER		40
OCTANE NUMBER		92
VISCOSITY		4.5 MM2/SEC

TABLE II. REBOILER TEMPERATURE VS CONVERSION

TEMPERATURE	% METHYL ESTER
50°C	20
75°C	90
100°C	100
125°C	100

Methanol: WCO - 6:1

n-hexane : 10% by volume

Flow rate of WCO : 1 (ml/min)

Residence time : 5 mins

TABLE III. OPTIMUM FLOWRATE OF WCO

FLOWRATE OF WCO	% METHYL ESTER
1 ML/MIN	98
1.5 ML/MIN	95
2 ML/MIN	92
2.5 ML/MIN	90

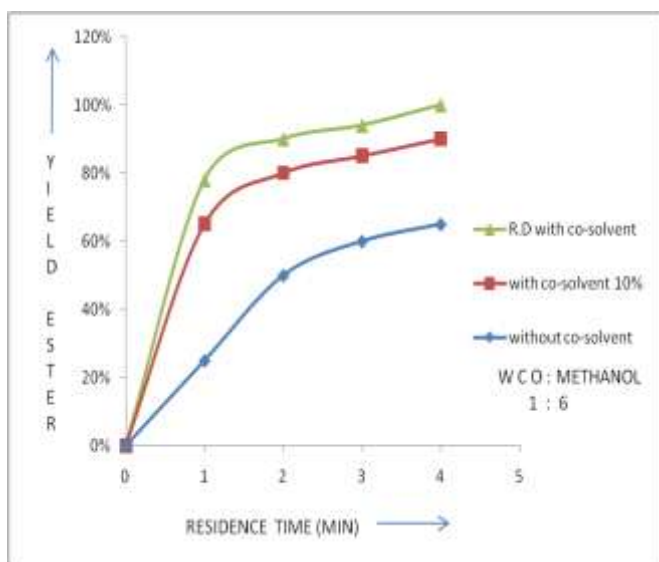
Methanol: WCO - 6:1  
 n-hexane : 10% by volume  
 Residence time : 5 mins

TABLE IV. OPTIMUM RESIDENCE TIME

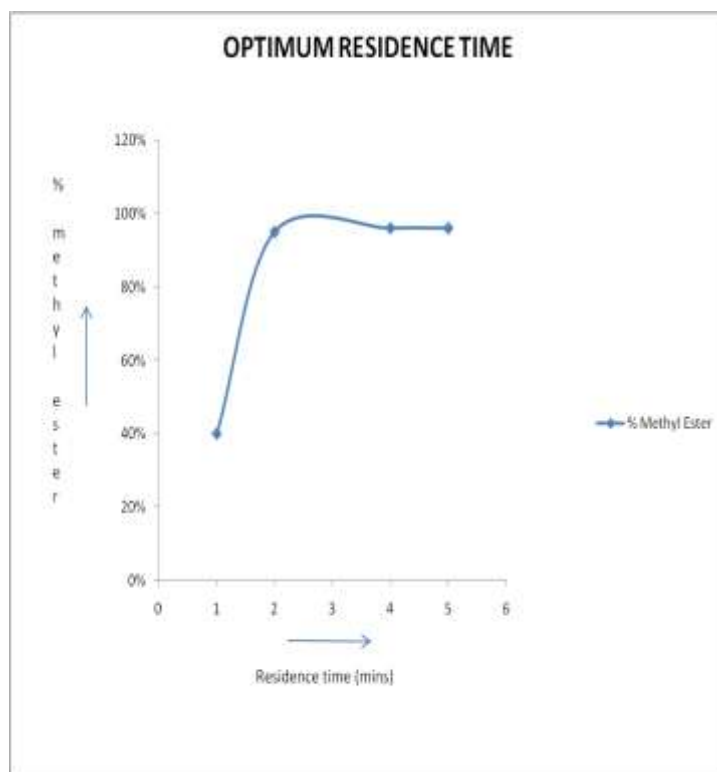
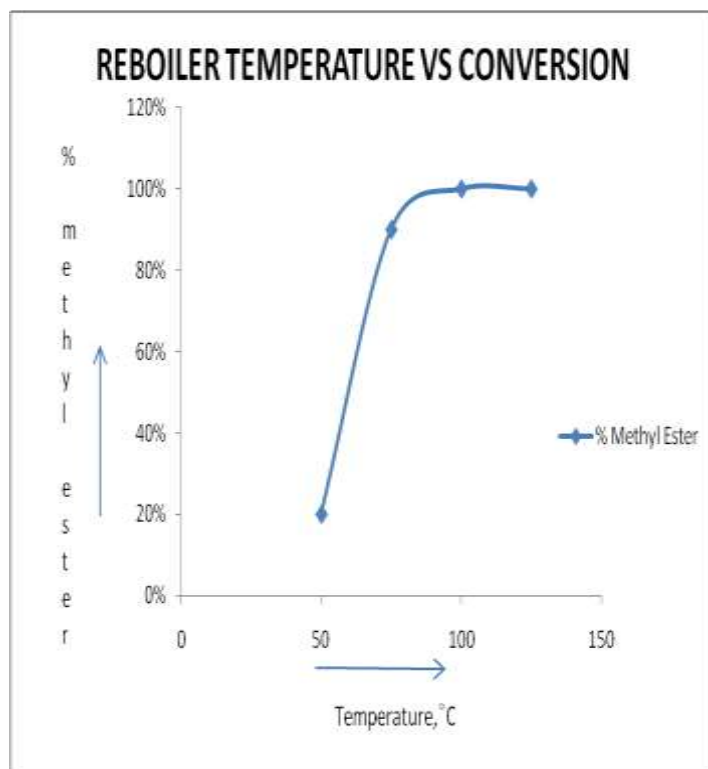
RESIDENCE TIME	% METHYL ESTER
1 MIN	80
2 MIN	85
4 MIN	96
5 MIN	98

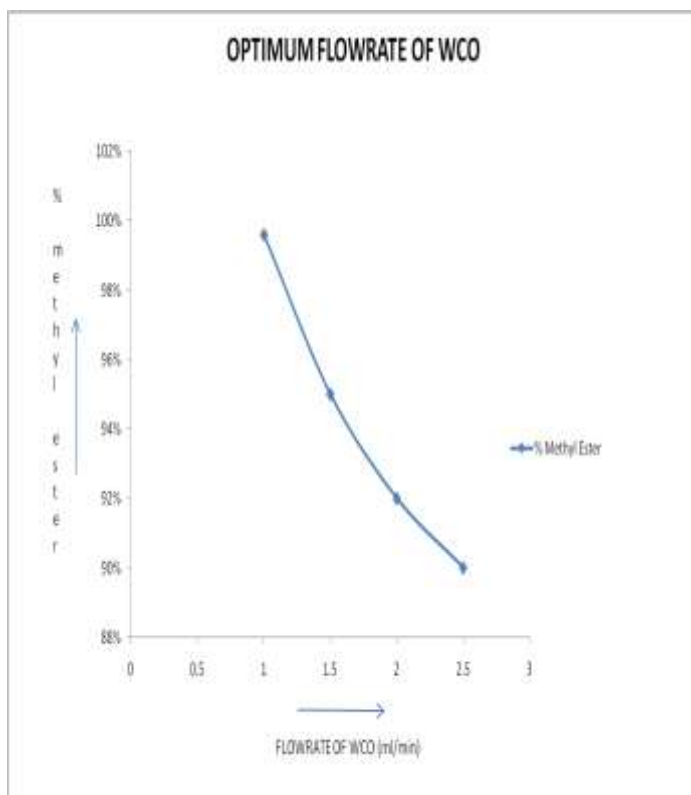
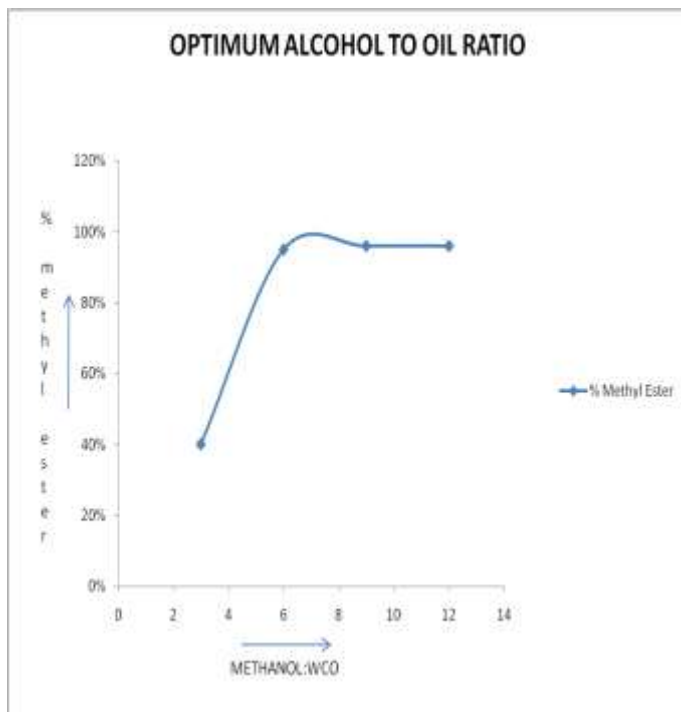
Methanol: WCO - 6:1  
 n-hexane : 10% by volume  
 Flow rate of WCO : 1 (ml/min)

GRAPH I. COMPARISON OF TRANSESTERIFICATION, CO-SOLVENT TRANSESTERIFICATION AND TRANSESTERIFICATION WITH R.D



GRAPH II. VARIATION OF % YIELD OF ESTER FOR DIFFERENT OPERATING PARAMETERS





## CONCLUSION

Reactive distillation eliminates separating units and has possibility of 100% conversion. Selectivity of the desired products enhanced as one of the reactants is removed. Catalyst requirement for the same degree of conversion is less compared to conventional reactors. Hotspots eliminated as liquid is vapourised and circulated. In the transesterification of WCO using methanol and n-hexane as co-solvents, the reaction is carried out in the single phase. Methyl ester yield, reaction temperature, reaction time and solvent recovery enhanced by using Reactive Distillation. This study helps to identify the reaction zone, fractionation zone and rectification zone in the process of designing and sizing of transesterification plants using co-solvent.

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## Symbols Used

$A_i$	Component i
$c_i$ kmol/m <sup>3</sup>	Component concentration
$k_1$ $\frac{m^3}{kmole \cdot h}$	Rate constant for the forward reaction
$k_{-1}$ $\frac{m^3}{kmole \cdot h}$	Rate constant for the reverse reaction
$k_c$	Equilibrium constant
$\tau$ h	Residence time

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