Waste Oils pre-Esterification for Biodiesel Synthesis: Effect of Feed Moisture Contents

Kalala Jalama

Abstract—A process flowsheet was developed in ChemCad 6.4 to study the effect of feed moisture contents on the pre-esterification of waste oils. Waste oils were modelled as a mixture of triolein (90%), oleic acid (5%) and water (5%). The process mainly consisted of feed drying, pre-esterification reaction and methanol recovery. The results showed that the process energy requirements would be minimized when higher degrees of feed drying and higher pre-esterification reaction temperatures are used.

Keywords—Waste oils, moisture content, pre-esterification.

I. INTRODUCTION

THE decreases in crude oil reserves and environmental concerns have created a need for renewable energy sources. Biodiesel is one of the renewable energy sources and has received more attention in the past few years than ever before. However, the major challenge for biodiesel production is the high production costs compared to fossil diesel as shown by previous studies [1-4]. These studies have shown that the cost of feedstock is the major contributor to the high production cost of biodiesel. Significant amounts of water are required to grow the seed from which the feedstock for biodiesel production is extracted and dedicated land for growing the seed is required. This poses serious problems especially for regions where water resources are scarce and the land availability limited. Growing biodiesel feedstock competes with food production in terms land and water requirements. While this is overcome in certain regions, it is a major challenge in other regions where governments have simply ruled out biodiesel alternatives for food security. For these reasons, waste oils have received more attention as feedstock for biodiesel production for the past few years. These materials are almost free if the collection logistics are optimized and their use as feedstock also contributes to a better control of the environment. However the use of these waste oils is also associated with some challenges. They usually contain high amounts of free fatty acid (FFA) and moistures that favour side reactions such as soap formation in the oils transesterification reaction using base catalysts. Typical examples of FFA acid and moisture contents in waste oils are reported in Table I below.

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TABLE I
PROPERTIES OF CRUDE WASTE FRYER GREASE [5]

Property	Value
Solid portion	19%
Total polar compounds	22%
Polymerized triglycerides	1.43%
Oxidized triglycerides	4.72%
Acid value	11.2 mg KOH g^{-1}
Free fatty acid (FFA)	5.60%
Water content	7.30%
Saponification value	177.87 mg KOH g^{-1}

To avoid side reactions due to the presence of FFA in the feedstock an acid catalyzed transesterification or an alkali catalyzed process with an oil pre-esterification step can be considered. When alkali catalyzed transesterification is used, the feedstock used should not contain more than 1wt.% of FFA [6, 7] to avoid side reactions such as soap formation that would adversely affect subsequent separation processes. Low grade oils are usually pre-treated using acid catalysts to reduce the FFA contents to < 1% prior to the transesterification reaction. This process consists of direct esterification of the FFA acids with an alcohol, for example methanol, forming methyl ester and water. The effect of water on the esterification of FFA has been reported in literature [8, 9]. The rate of esterification was found to decrease upon increase in water contents. Yingying et al. [8] studied the pre-esterification of Jatropha curcas L oil before the alkali catalyzed transesterification reaction. They found that water remarkably lowered the catalytic activity of sulphuric acid due to the reduction of proton concentration and acid strength. Park et al. [9] studied the esterification of oleic acid and high acid acid oil (HAAO) by reaction with methanol over Amberlyst-15 as a heterogeneous catalyst or using sulfuric acid as a homogeneous catalyst. They explained the decrease in the Amberlyst-15 catalytic activity upon water content increase by direct poisoning of acid sites by water.

The esterification of FFA acids is an equilibrium reaction and factors such as water contents and reagents molar ratios (alcohol to FFA) would have a significant effect on the equilibrium conversion. Previous studies have mainly explained the water effect on the esterification of FFA more in terms of kinetics but have not shown how far from equilibrium were the measured FFA conversions upon the increase of water contents. Another study [10] looked at equilibrium conditions for the esterification of FFA but did not consider

the effect of water in the feed. Hence very limited information on the effect of water on the equilibrium conditions for the FFA esterification is reported in literature.

In the present paper we report the effect of the water contents of simulated waste oil as the feed material to a pre-esterification process before an alkali catalyzed transesterification process. The esterification reaction temperature, the alcohol to waste oil ratios required to reduce the FFA contents in the waste oil to < 1wt.% as a function of water contents in the feed and the process energy requirements will be determined.

II. METHODOLOGY

A. Process flowsheet

The flowsheet developed for this study is presented in Fig. 1. Waste oil (1000 kg/h) was pumped to a heat exchanger E-1 using a pump P-1. The waste oil was heated and flashed in a drum F-1 after depressurization through a valve V-1 to remove the moisture from the oil. The delivery pressure of P-1 and the heat duty for E-1 were adjusted to achieve various degrees of waste oil drying. The removed moisture left the flash drum through stream 05. The dried oil was cooled to 60°C by a heat exchanger E-2 and pumped by a pump P-2 to the mixing unit M-1 where it was mixed with methanol containing sulphuric acid catalyst (30 kg/h of H_2SO_4) and pumped using a pump P-3. The mixer outlet was pumped to the esterification reactor (R-1) using a pump P-4. The delivery pressure for P-4 was adjusted to keep the methanol in liquid phase in the reactor when the operating temperature was above its normal boiling point. The esterification reactor outlet was depressurized through a valve V-2 and sent to a methanol recovery distillation column C-1. The C-1 bottoms were sent to subsequent processing such as acid neutralization and transesterification, not covered in this study.

B. Feed conditions

A model waste oil containing 5wt.% FFA and 5wt.% moisture has been used. The moisture contents in the feed to the esterification reactor were varied from 5 to 4, 3, 2 and 1 wt.% respectively by introducing a drying unit in the process flowsheet in order to also evaluate the energy requirements for the drying process. A waste oil feed with no water contents was also considered for reference.

The waste oil feed flowrate was set at 1000 kg/h before drying.

The moisture content in the feed was expressed as follows:

$$Moisture \ \% = \frac{\left(mass \ rate \ of \ H_2O \ in \ the \ feed\right)\times100\%}{total \ mass \ rate \ of \ the \ feed} \quad (1)$$

The methanol to waste oil molar ratio was based on dried oil feed and was defined as:

$$MeOH/Waste \ oil \ molar \ ratio = \frac{molar \ rate \ of \ methanol \ in \ stream \ 10}{molar \ rate \ of \left(triolein+oleic \ acid\right) \ in \ stream \ 08} \quad (2)$$

C. Components selection and property model

The following components were available in the ChemCad components database and were used in the FFA pre-esterification process simulation:

1. Triolein was used to model the triglycerides in waste oil;
2. Oleic acid was used to model the FFA in waste oil;
3. Methyl oleate was used to model the fatty acid methyl esters (FAME)/biodiesel;
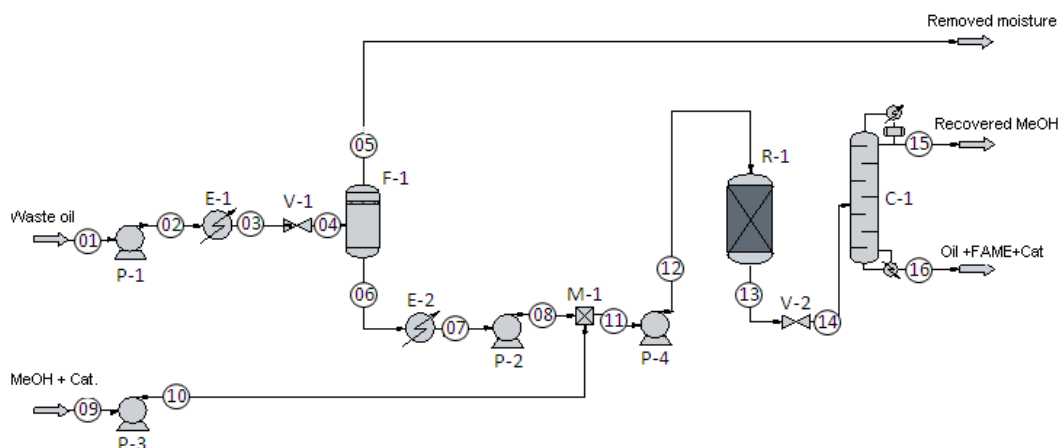4. Methanol;
5. Water;
6. Sulphuric acid.

Fig. 1 Process flowsheet used for the study

As a two-phase system was predicted, NRTL was used as property model. All missing binary interaction parameters (BIP) were regressed using UNIFAC LLE.

D. Esterification reaction

The FFA esterification reaction was modeled assuming equilibrium conditions.

Sulfuric acid was selected as catalyst for the waste oil pre-esterification reaction. Zheng et al. [11] reported the time course for products formation during sulphuric acid catalyzed *trans*-esterification of waste oil (canola oil, derived from rapeseed oil) containing 6 wt.% of free fatty acid with methanol at 80°C with a methanol to oil ratio of 74:1. The FFA in the waste oil was rapidly converted to fatty acid methyl esther in a fraction of a minute and they could not detect any FFA in the reaction sample taken after 0.5 min of reaction. Their results showed that the FFA esterification was far much faster as it happened in less than a minute compared to the *trans*-esterification reaction of triglycerides in the waste oil that required about 4 hours to be completed. Other studies [6, 12] also showed that when an acid catalyst was used, the *trans*-esterification of triglycerides was very slow and required longer hours to reach higher conversions. For example Freedman et al. [12] reported that the *trans*-esterification of soybean oil with methanol (molar methanol to oil ratio of 30:1) in the presence of 1 mol.% of H_2SO_4 at 65°C took 50 hours to get to completion. These earlier reports suggest that FFA esterification in presence of an acid catalyst can indeed be fast and reach equilibrium while almost of the triglycerides are still unconverted to FAME through *trans*-esterification. Hence in this study, we have assumed conditions where the reactants residence times in the reactor were such that the FFA acid esterification got to equilibrium while almost no *trans*-esterification of triglycerides happened.

The FFA conversion was calculated as follows:

$$FFA\,conv. = \frac{mass\ rate\ of\ FFA\ in\ stream\,12 - mass\ rate\ of\ FFA\ in\ stream\,13}{mass\ rate\ of\ FFA\ in\ stream\,12} \quad (3)$$

E. Methanol recovery

Methanol recovery was modeled using a rigorous distillation method in ChemCad. A shortcut method based on Fenske empirical model was first used to determine the minimum number of stages from which the required number of stages and the feed stage location were determined using an R/Rmin ratio of 1.30. These number of stages, feed stage location and reflux ratio were input to a rigorous distillation column model SCDS in ChemCad.

III. RESULTS AND DISCUSSION

The effect of the moisture content in the waste oil feed on the equilibrium conversion of the FFA in the pre-esterification reaction was evaluated at reaction temperatures of 60, 80, 100 and 120°C and with various methanol to oil molar ratios from 3 to ca. 120. The results are summarised in Fig. 2 below. For the reaction performed at 60°C (Fig. 2a) an equilibrium fractional conversion of ca. 0.55 was achieved with a moisture-free feed with a methanol to oil ratio of 3:1.

At similar conditions, lower fractional equilibrium conversions of 0.18, 0.09 and 0.08 were respectively measured for the feed containing 1, 3 and 5 % moisture. Increasing the methanol to oil ratios increased the equilibrium conversions as this could be predicted from the Le Chatelier principle. No significant increase in equilibrium conversion were noted above a methanol to oil ratio of ca. 30:1 for the reaction with the moisture-free feed. This value shifted to ca. 22, 20 and 18 respectively for reactions performed at 80 (Fig. 2b), 100 (Fig. 2c) and 120°C (Fig. 2d). The overall trend of the data presented in Fig. 2 shows that the equilibrium conversion increases with both the reaction temperature and the methanol to oil ratio. When compared at the same reaction temperature and methanol to oil ratio, the equilibrium conversion increases with a decrease in the feed moisture constant. This is because water is formed in the esterification reaction and will adversely affect the equilibrium constants as per the Le Chatelier principle.
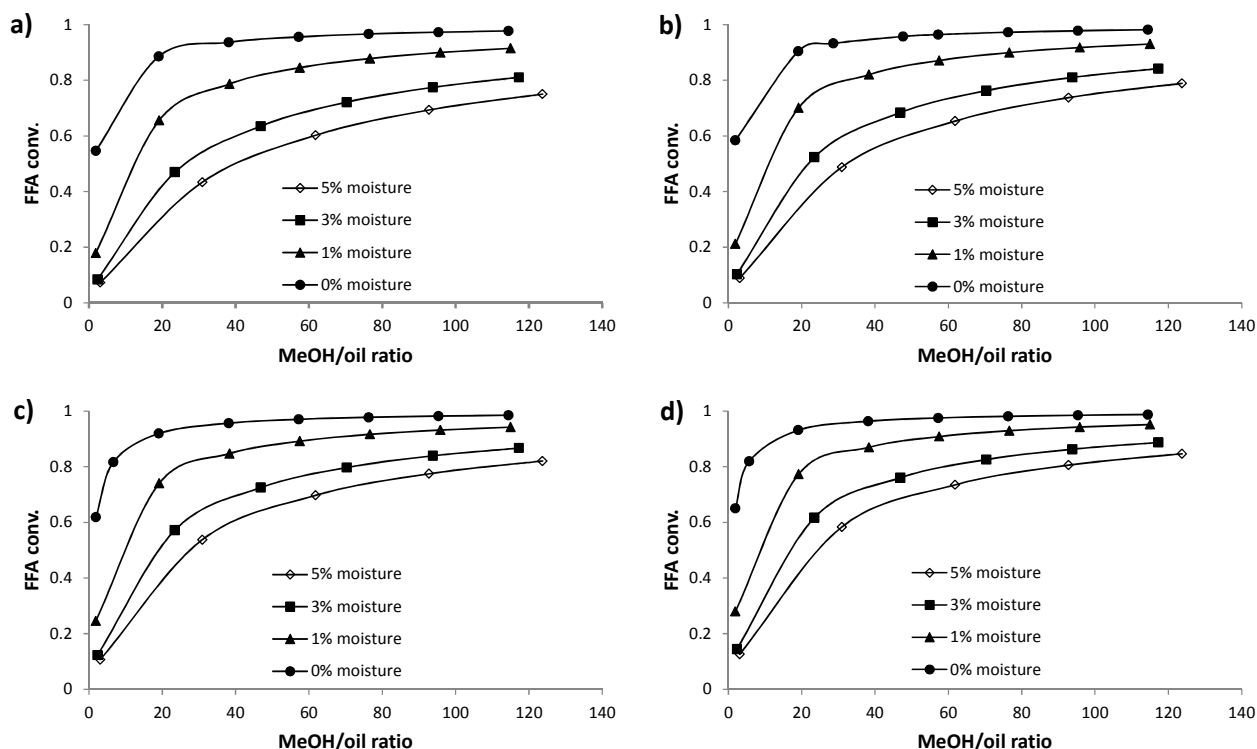
Fig. 2 Effect of water content (effect of feed drying) in the feed on equilibrium conversion as a function of MeOH to oil ratio at different reaction temperatures: a) 60°C; b) 80°C; c) 100°C and d) 120°C

In other to reduce the moisture content to below 1 wt.% in the feed, FFA conversions of ca. 82% were required. The minimum methanol/oil ratio and the reaction temperature required for these conversions are summarised in Fig. 3.
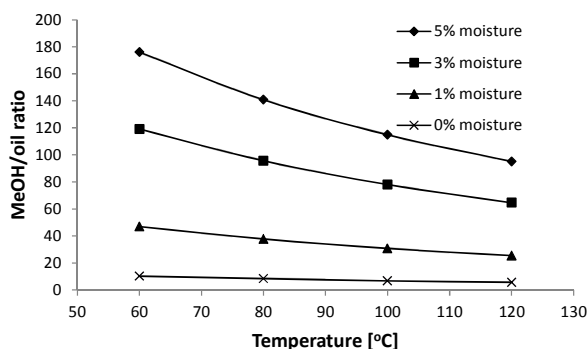

Fig. 3 Effect of water content in the feed on the methanol/oil ratio and temperatures required to reduce the FFA contents to below 1wt.% in the esterification reactor exit.

These data suggest that for a fixed feed moisture content huge methanol/oil ratios will be required to reduce the FFA contents below 1 wt.%. A way to avoid these huge methanol/oil ratios will be to operate at a higher reaction temperature with a feed that contains minimum moisture. The process of reducing the feed moisture to its minimum also requires energy. Table II reports the energy required to achieve various degree of feed drying based on assumptions made in section B.

TABLE II
ENERGY REQUIREMENTS FOR DIFFERENT LEVELS OF MOISTURE REMOVAL
FROM THE WASTE OIL FEED

% water removed from the feed	Energy required [MJ/h]
10	36.72
20	47.92
40	74.6
60	97.5
80	124.58

The energy required is directly proportional to the degree of drying required.

The energy requirements for the flowsheet developed in this study will mainly be a resultant of the energy required by: i) the feed drying, ii) the FFA esterification reaction at required temperature and iii) the methanol recovery that is mainly determined by the reboiler duty for the methanol recovery column. These requirements vary in different directions and make it difficult to determine the optimal conditions to minimize the energy requirements for the process. Fig. 4 shows a summary of a sensitivity analysis where the process energy requirements and distribution are determined as

function of the degree of drying for the feed and the reaction temperature. These data suggest that the process energy requirements will be minimized when higher degrees of drying are achieved in the feed and higher FFA esterification reaction temperatures are used.
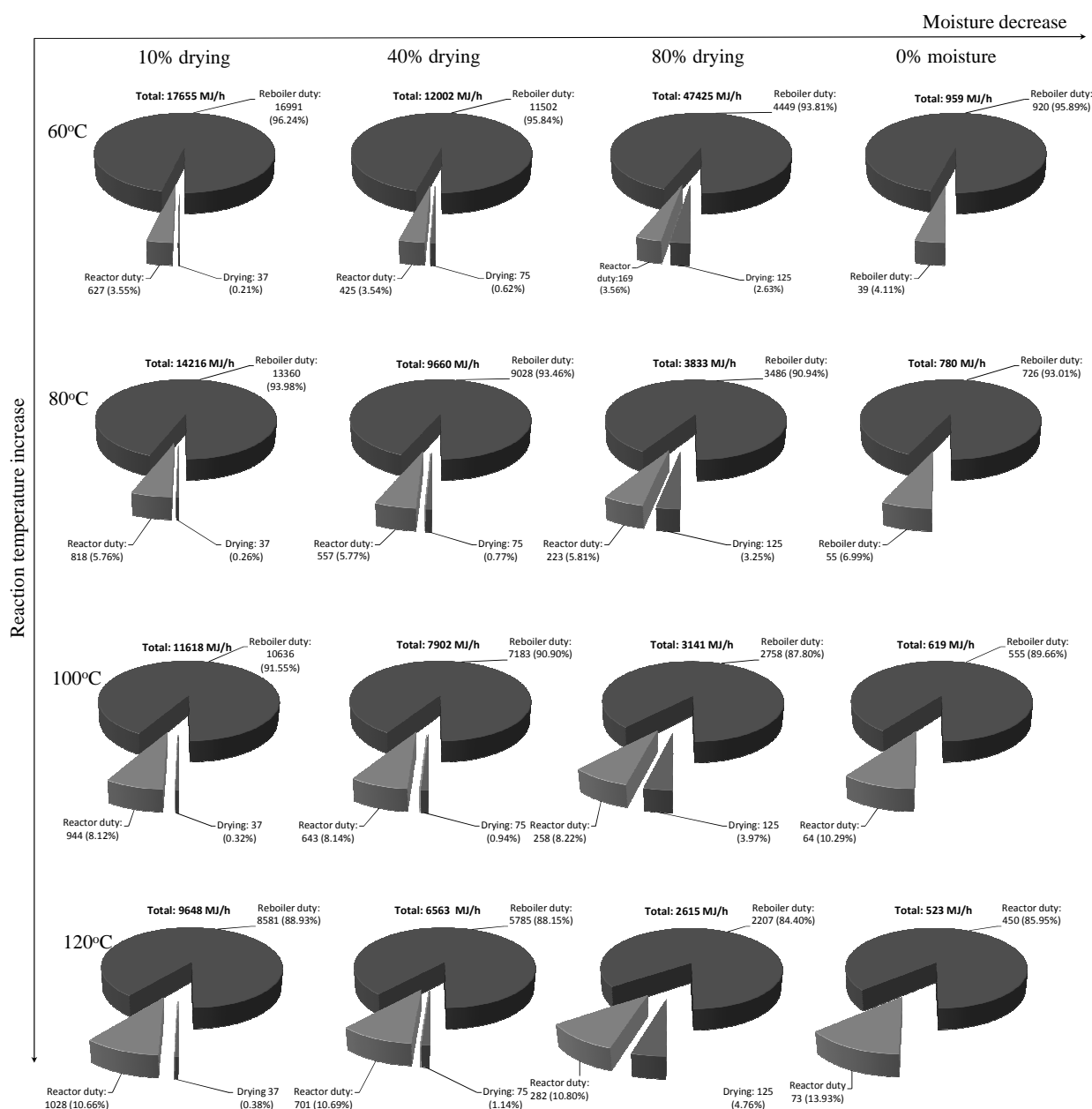

Fig. 4 Summary of energy requirements as function of reaction temperature and degree of feed drying

IV. CONCLUSION

The effect of moisture contents on the pre-esterification of waste oils has been evaluated using ChemCad 6.4 simulation package. The waste oil was modeled by a mixture of triolein to represent the triglycerides and oleic acid (5%) to represent the FFA. The waste oil feed was assumed to contain 5% moisture.

NRTL property model was selected for the simulation study and all the missing BIP was regressed using UNIFAC LLE.The process consisted of feed drying, transesterification reaction, and methanol recovery. A sensitivity analysis on the effect of feed drying levels and reaction temperature on the process energy requirements has revealed that process energy requirements would be minimized when higher degrees of feed drying and higher reaction temperatures are used.

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