SYMPOSIUM SERIES NO. 152 © 2006 IChemE

BIODIESEL PRODUCTION, LUBRICANT FRACTIONATING AND DEVELOPMENT OF A NEW TRUE BOILING POINT CURVE THROUGH MOLECULAR DISTILLATION

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Biodiesel is an alternative biodegradable and nontoxic fuel, which is essentially free of sulfur and aromatics. This work presents the transesterification process of castor oil with ethanol in the presence of sodium ethoxide as catalyst, because it leads to better conversion and smaller reaction time.

Chemically, this oil contains approximately 90% of ricinoleic acid, which gives to the oil some important characteristics, such as its ethanol solubility at 30°C, allowing reaction at low temperature.

The ester conversion was determined through high-performance size-exclusion chromatography, also called gel-permeation chromatography.

Good phase separation was obtained with the methodology developed. The best experimental operating conditions to obtain high conversion, in terms of temperature, molar ratio ethanol/castor oil were identified. The success of the developed process is also due to the proposed separation scheme.

As a second objective of this work, lubricant fractionating through molecular distillation process was developed. Important recoveries were found in both streams of the molecular distillation: distillate and residue.

Petroleum is evaluated mainly in terms of its True Boiling Point (TBP) curve, what makes possible to investigate the yields of the products that will be obtained in the refineries, as well as to establish operational strategies and process optimization. The determination of TBP is well established for petroleum fractions that reach the TBP up to 565°C through ASTM. Even so, for higher temperatures, there is not yet a standard methodology. In this way, methodologies were established for the determination of the true boiling point for heavy fractions of petroleum above 565°C, where it was possible to reach values up to 720°C, representing a considerable progress in the analyses of heavy petroleum fractions. Through falling film molecular distillation apparatus, experiments were carried-out using heavy fractions of petroleum, where operating temperatures were increased systematically. The fractions obtained in each one of the pre-established temperatures were collected, quantified and characterized for both streams of the distillation apparatus. With this information, plus the process conditions of the molecular distillation, and with the physical characterization of the materials, the Framol correlation was used in order to determine accurately and appropriately the true boiling points for each studied heavy petroleum fraction. These three examples show developments in terms of energy efficiency and sustainability.

INTRODUCTION

Biodiesel is produced through transesterification reaction of vegetable oils and animal fats preferentially with alcohol of low molecular weight. Ethanol is an alternative to methanol, because it allows production of entirely renewable fuel. This reaction can be carried out in presence of alkaline or acid catalysts.

Alkaline transesterification of castor oil has been studied in the literature (Oliveira *et al.*, 2005; Smith, 1949; Meneghetti *et al.*, 2004; Ma and Hanna, 1999 and Cotes *et al.*, 1974). Oliveira *et al.* (2005) use a relatively small castor oil:ethanol molar ratio (1:3–1:9). However, it is not clear how the authors got the decanted phase and the phase separation.

In this work, the ethanol/castor oil molar ratios were different from those ones, and very good results were achieved with the proposed conditions, mainly in the separation stage of the process. Initially, smaller ratios (6:1–9:1) were considered, however phase separation was not possible (indeed, a kind of gel, was obtained). These results are in accordance with the work of Meneghetti *et al.* (2004).

Castor oil has a proper characteristic that is its composition of 90% of ricinoleic acid. The castor oil is the best substance for producing biodiesel, because it is the unique that is soluble in alcohol, and it does not require heat and the consequent energy requirement of other vegetable oils in transforming them into fuel (Beltrão, 2005).

Different variables affect the castor oil transesterification such as reaction temperature, ethanol: castor oil molar ratio, catalyst concentration, level of agitation and reaction time. Response-surface methodology (RSM) was used, because it allows the simultaneous consideration of many variables at different conditions and the interactions between them, using a smaller number of observations than conventional procedures (Mason, 1989).

Molecular distillation is useful for processes that demands high purity and quality. Since it does not require the use of solvents and operates at low pressures (high vacuum), it allows using low temperatures avoiding material thermal degradation. Furthermore, the small distance between the evaporator and the condenser is a crucial point in the design of such equipments, playing an important role in the process performance.

Molecular distillation involves, basically, two stages: evaporation and condensation, in which vapor molecules escape from the evaporator in direction to the condenser, where condensation occurs. It is necessary that the vapor molecules generated find a free path between the evaporator and the condenser, the pressure be low and the condenser be separated from the evaporator by a smaller distance than the mean free path of the evaporating molecules (Batistella and Wolf Maciel, 1998; Batistella et al., 2000; Batistella et al., 2001a,b; Moraes et al., 2004). Moreover, the product flow rates generated are technologically viable (Batistella et al., 2000; Lutisan et al., 2000). Since heavy petroleum fractions have high molecular weight and are easily cracked, and the purification of

biodiesel by-product is economically very important, the process conditions above mentioned allow to apply this technique successfully.

Since it is a multivariable process, in order to obtain high performance operation, it is important to define a suitable strategy focused on the product desired characteristics, identifying the effect of each process variable. Furthermore, the interactions among them should be understood and taken into account in the process development.

The properties of natural petroleum and petroleum products make use of the True Boiling Point (TBP) distillation analysis and this is very useful for design and operation of refinery units, contributing to the petroleum science and technology, to the classification of petroleum, to the development of petroleum property correlations and it has been used worldwide. However, when applied to heavy petroleum fractions, difficulties are often encountered (Yang and Wang, 1999).

Usually, the evaluation of the TBP curve of heavy petroleum fractions has been carried out through ASTM D2892 and D5236 methods, but values are limited to temperatures below 565°C. For higher temperatures, a well established method does not exist, although this is a very important achievement, in order to improve the crude oil processing.

On the other hand, large amounts of crudes processed in oil refineries are set aside as distillation residue. At present, these residues are of relatively poor commercial value. More detailed structural characterizations are necessary before to improve process routes to upgrade these materials, to lead them to have added values (Suelves et al., 2003).

In this work, the fractionating of two lubricant oils, called here Alpha and Beta (fantasy names), were studied using the falling film molecular distillator. This process was used also for extending the TBP curve (above 565°C) of a heavy petroleum (called here Alpha), in order to use it for characterizing vacuum residues of such oil. This is of great importance for the optimization of refining processes and environmental issues. Also, the ASTM D1160 will be adapted for high vacuum for heavy petroleum application. Framol correlation was used for extending the TBP curve. Besides that, glycerol was purified using this separation process.

MATERIALS AND APPARATUS
BIODIESEL PRODUCTION
Castor oil with free fatty acid of 0.25%, anhydrous ethanol from Merck and sodium ethoxide from Aldrich 95% pure were used. The experiments were carried out in a 250 ml flask, connected with a condenser. The system was kept at normal pressure and the experiments were carried out at constant temperature. The agitation was kept constant at 600 rpm. The reaction time was 90 minutes, and during this time, samples were collected and analyzed in the HPSEC (high-performance size-exclusion chromatography).

After reaction, a rota-evaporator was used in order to recover the ethanol excess and the mixture was placed in a separation funnel. After some time, which depends on the composition of the mixture, and at room temperature, two layers are formed: the upper

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one rich in ester and the lower one rich in glycerol, catalyst and some impurities. Later, the ester phase was separated. The ester phase is continuously washed using acidified water up to get the neutral condition. Following, this mixture is put in a separation funnel in order to remove excess of water glycerol was purified by molecular distillation.

FALLING FILM MOLECULAR DISTILLATOR

The basic design of the falling film molecular distillator unit is the Short Path Distillation unit: a vertical, double jacketed cylinder (evaporator) with a cooled and centered internal condenser and in the annular physical space there exists vacuum, normally in the order of 10^{-3} mmHg. In the walls of the evaporator, an agitation shovel promotes the uniformity of the film formed. The feed is placed in a heated tank, with gear pump. Rotating carousels holding discharge sample collectors for distillate and residue streams are present (each carousel consists of 6 collectors which can be positioned and moved by the operator without interrupting the distillation process). The equipment has a set of vacuum pumps with an in-line low temperature cold trap and four heating units.

RESULTS AND DISCUSSION

BIODIESEL PRODUCTION

The factors (designated as X_i) are proper nomenclature of experimental design (Box, 1978). They were set independently of each other within the following limits: temperature (X_1): $30°C \leq T \leq 80°C$; catalyst concentration (X_2): $0.5\% \leq C \leq 1.5\%$, by weight of castor oil; ethanol:castor oil molar ratio (X_3): $12:1 \leq E:O \leq 20:1$ (Lima Silva *et al.*, 2006). A total of 17 experiments were carried out as shown in Table 1 and the reaction time was 90 minutes. The maximum ester conversion (Y) was 93.03% at 70°C, 1.3%wt of catalyst concentration and E:O equal to 13.6:1.

As shown in Figure 1, a plot of conversion (Y) to ethyl ester vs. time, the reaction is very fast, and conversions larger than 90% are reached within 15 min, however, the time was considered up to 90 min.

LUBRICANT FRACTIONATING

Molecular distillation process is used to evaluate the behavior of the response variable (% distilled) in function of the process variables, such as, evaporator temperature (Tevap), condenser temperature (Tcond), feed flow rate, feed temperature (Tfeed) and agitation inside the apparatus.

A Fractional Factorial Design 2^{5-1} and a Factorial Design 2^3 are considered, both with central points (Box, 1978). Each stage of distillation was carried out at constant pressure (10^{-3} mbar) and produced one cut of distilled and another one of residue. The studied ranges in this work were: feed temperature from 80 to 100°C, evaporator temperature from 90 to 140°C, condenser temperature from 40 to 60°C, feed flow rate from 300 to 600 mL/h and agitation from 250 to 450 rpm.

Figure 2 shows the Pareto chart of effects of Tevap, Tcond, feed flow rate, Tfeed and agitation on the response variable (% distilled) for lubricant Alpha. In Figure 3 based on

Table 1. Ethyl ester conversion of castor oil transesterification

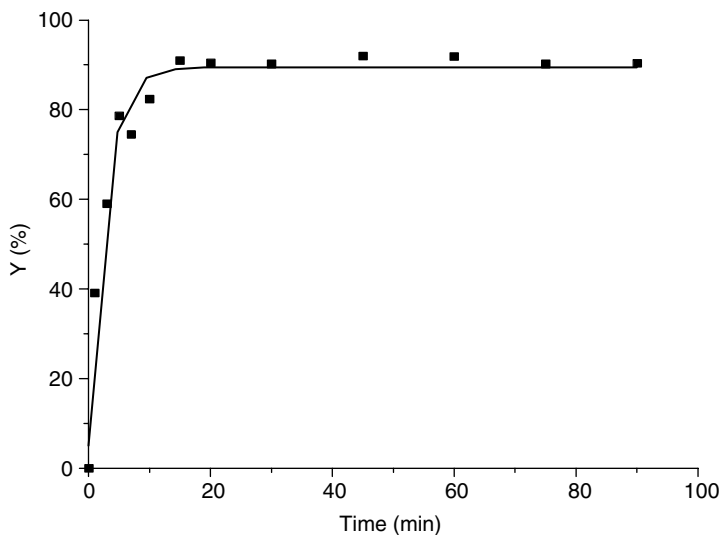| Experiment	X_1	X_2	X_3	Conversion (%)
1	40°C	0.7%	13.6:1	53.30
2	70°C	0.7%	13.6:1	63.29
3	40°C	1.3%	13.6:1	90.99
4	70°C	1.3%	13.6:1	93.03
5	40°C	0.7%	18.88:1	81.39
6	70°C	0.7%	18.88:1	70.47
7	40°C	1.3%	18.88:1	90.85
8	70°C	1.3%	18.88:1	91.31
9	30°C	1.0%	16:1	90.44
10	80°C	1.0%	16:1	91.80
11	55°C	0.5%	16:1	48.40
12	55°C	1.5%	16:1	88.39
13	55°C	1.0%	12:1	83.42
14	55°C	1.0%	20:1	90.02
15	55°C	1.0%	16:1	89.99
16	55°C	1.0%	16:1	89.51
17	55°C	1.0%	16:1	89.75

Figure 1. Conversion to ethyl ester vs. time. Catalyst: NaOEt; T = 30°C; C = 1 wt%; E:O = 19:1
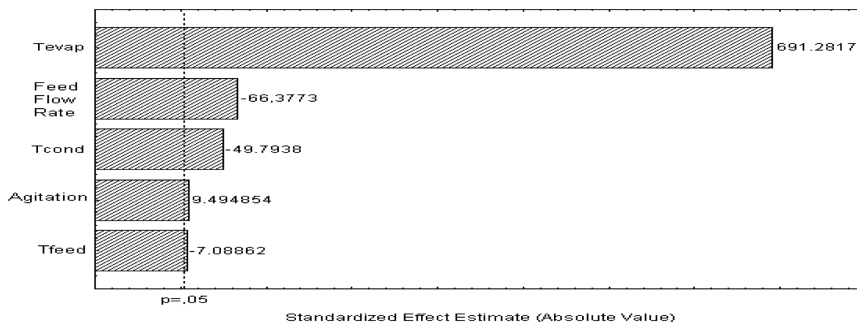
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Figure 2. Pareto chart for lubricant Alpha (pure error = 0.0532)

the information taken from Figure 2 the following variables were considered: Tevap, feed flow rate, Tcond, the interaction feed flow rate by Tevap, the interaction Tevap by Tcond and the interaction feed flow rate by Tcond.

Analyzing the figures, the largest influence on the % distilled is the evaporator temperature, followed by feed flow rate, after by the interaction between Tevap and feed flow rate followed of the condenser temperature for 95% of confidence (p = 0.05). The interactions involving Tcond, practically, do not have influence on the response variable for the range studied.

DETERMINATION OF THE TBP FOR PETROLEUM ALPHA
The distillation curve was determined, for ASTM D1160, from the temperature and the percentage of distillate obtained experimentally but, in the case of this work using molecular distillation. This is a new procedure to build-up this curve. The relationship between
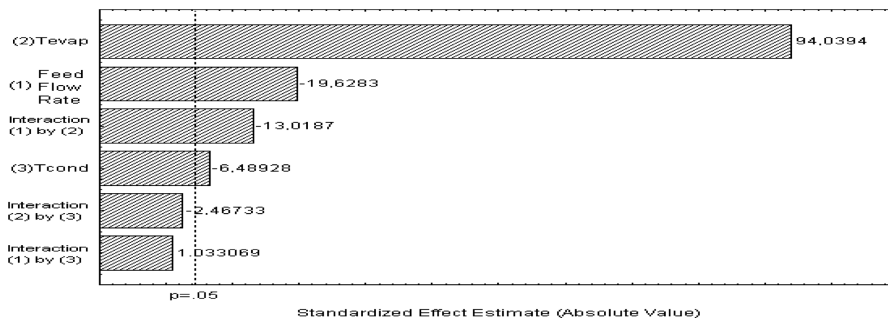

Figure 3. Pareto chart for lubricant Beta (pure error = 0.4970)

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the operating conditions from Molecular Distillation and the data obtained from the Atmospheric Column (industrial data) generates the extension of the TBP curve, which was analyzed in this work.

Figure 4 shows the TBP curve determined for the ASTM and the methodology developed in the present work for Alfa (fantasy name) petroleum. The extension of TBP curve reached approximately 700°C. The extension presents continuity and good agreement with the ASTM curve. However, evaluating the projected curves for values of cut tending to 100% (Figure 5), it is possible to verify that the trend of the curve goes for an asymptotical, while the extrapolation of TBP curve obtained with ASTM correlation tends to stabilize, and the extension is not observed in the adjustment of the correlation with the ASTM data. So, the extension provided a good adjustment including the values of TBP above 700°C.
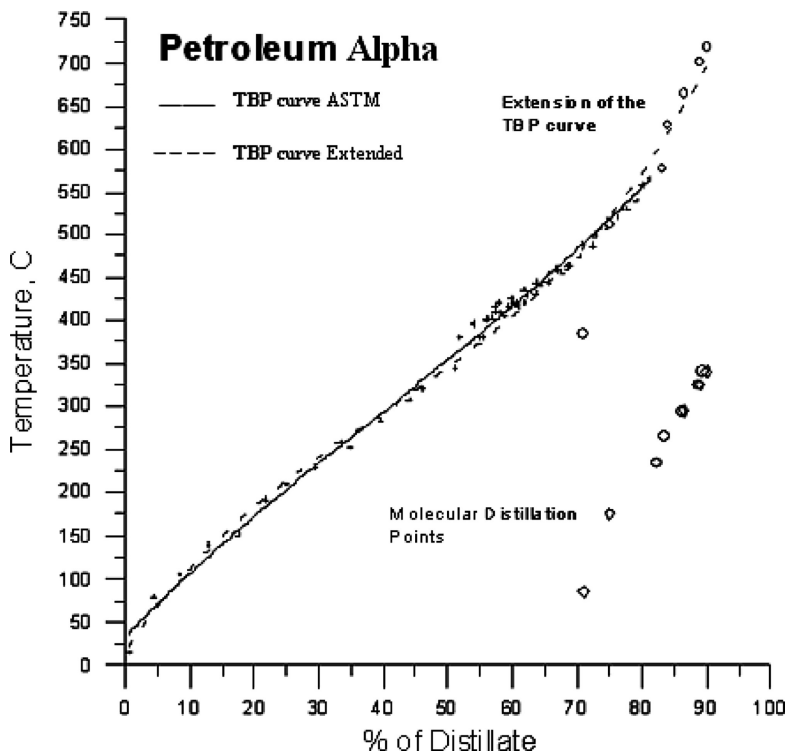

Figure 4. True boiling point curve and extension for ASTM D1160 and considering FRAMOL correlation for the vacuum residue Alpha
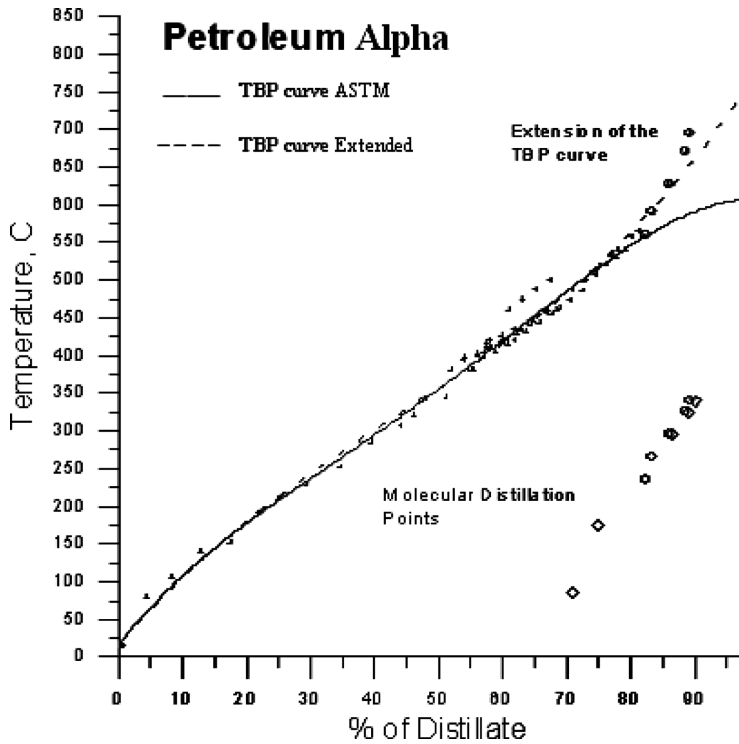
Figure 5. True boiling point curve and extension tending to the 100% of destillation for ASTM D1160 and considering FRAMOL correlation for the vacuum residue Alpha

Furthermore, it can be seen in Table 2, that the use of molecular distillation also enabled to obtain better improvement of the crude oil (gain of about 10% in distillate).

$$TBP = 456{,}4 + 0{,}1677 \times T_{DM} + 1{,}64.10^{-4} \times T_{DM}^{2} + 4{,}13.10^{-6} \times T_{DM}^{3} \qquad (1)$$

where:

TBP = True Boiling Point (°C);
T_{DM} = Molecular Distillator Temperature(°C).

Regarding to the results obtained, it is possible to extend the TBP curve through Molecular Distillation process with very good precision using the FRAMOL correlation (equation 1) and this is very important to define better strategies and operating conditions for the

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Table 2. Improvement obtained through Molecular Distillation in percentage of distillate accumulated

Kind of Brazilian petroleum	Percentage of distillate accumulated
Alpha	10

petroleum processing, with better economical use of heavy petroleum, as for example, in lighter components and asphalt, valuing this kind of petroleum due to its better characterization.

CONCLUSIONS

The developments achieved in this work are very important regarding to separation/ characterization of complex mixtures. In relation to biodiesel production, among the three parameters studied, catalyst concentration is the most important transesterification variable, although all of them increase the ester conversion, because they have positive influence on the response.

The experiments with lubricants show a larger influence of the evaporator temperature on the distilled percentage and are important for optimization of future experiments of molecular distillation with petroleum and its derivatives.

Molecular Distillation process made possible the extension of TBP curve with very good precision using the FRAMOL correlation and this is very important to define better strategies and operating conditions for the petroleum processing, with better economical use of heavy petroleum, as for example, in lighter components and asphalt, valuing this kind of petroleum due to its better characterization. The developments achieved in this work are very important since no standard methodology is available for calculating the TBP extended curve, considering the large amount of heavy petroleum today encountered.

These three examples show developments in terms of energy efficiency and sustainability.

AKNOWLEDGEMENT

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