The Optimum Operating Parameters for the Production of Biodiesel Using Reactive Distillation Technology

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Abstract

In this study, the production of biodiesel by using a laboratory-scale reactive distillation system is investigated. Two parent types of zeolite catalysts (NaX and Na5A) were used for the tranesterification of methanol and oil to produce methyl ester. Each type of zeolite was modified by exchanging Na^+ for Mg^+ and Ca^+ to form MgX, CaX, Mg5A, and Ca5A catalysts.

The packed reactive distillation column was made of Perspex glass with inner diameter of 2.5 cm and 60cm high divided into three zones: stripping zone = 15 cm, reaction zone= 15 cm, and rectification zone = 30 cm. The rectifying and stripping zones of the column were packed with rushing ring glass packing of 6 mm height, and 4, 6 mm inner and outer diameter respectively, while the reactive zone was packed with catalyst.

The effect of catalyst type on overall conversion was determined in reactive distillation column. Therefore, for all experiments, the performance of the catalysts was investigated by running the column at constant reaction temperature of 65 ^{o}C, atmospheric pressure, and total reflux ratio. The results show that, the reactive distillation technique can be used to produce biodiesel successfully with heterogeneous solid catalysts. From the six types of catalysts that were used in present work, it was concluded that the modified CaX catalyst is a suitable alternative to perform the transesterification reaction with good results and has better final conversion of about 92 % than other types.

It was concluded that the methanol/oil molar ratio of 4 gives the best results of biodiesel production (94 wt%). On the other hand, the physical properties and specifications of the prepared biodiesel meet the standards for diesel fuel and biodiesel.

Keywords: Biodiesel; reactive distillation; optimum preparation conditions.

1. **Introduction**

The consumption of fossil fuels increases the greenhouse gas emissions and cause global warming. Moreover, the diesel engines produce large amounts of small particulate matter that contaminate the atmosphere. Therefore, the need for a biodiesel is more pronounced today. This fuel can be used either straight or in varying proportions with petroleum diesel. The advantages of biodiesel are that the source of the oil is renewable, it burns more cleanly, and is less hazardous to the environment [1, 2].

Biodiesel (Fatty Acid Methyl Ester; FAME) is synthesized by the transesterification of vegetable oils or animal fat sources with low molecular weight alcohols like ethanol and methanol. The reaction is conducted in the presence of an alkaline catalyst to produce fatty acid esters. The homogeneous base catalysts, such as NaOH and KOH, are generally used for the industrial production of biodiesel. In the process, however, the undesired side reaction, saponification, occurs and an extra separation step to remove the homogeneous catalysts is required, thus reflecting the high cost of production [3, 4, 5]. Ni and Meunier [6] pointed to some disadvantages that are present in production of biodiesel that is catalyzed by homogeneous catalysts such as NaOH and KOH bases. Free fatty acids (FFA) are a strong poison to these catalysts and also lead to the formation of soap with the resulting separation difficulties. Therefore, they suggested using heterogeneous solid catalysts which are regarded the best solution for such disadvantages present with homogenous catalysts.

In recent years, reactive distillation provides an alternative to conventional processing schemes that include for instance a reactor followed by a distillation column in chemical production by combining reaction and separation. The reduction in the number of processing units and the direct heat integration between reaction and separation can reduce capital investment as well as utility costs. In practice, reactive distillation has found wide industrial applications through the continuous removal of desired products from the reaction zone of equilibrium limited reactions. Therefore, one the most important applications for this technology is the production of biodiesel [1, 7, 8].

There are several comprehensive studies of base catalyzed transesterification in the literature [2–8]. A number of articles relating to the development of heterogeneous catalysts for transesterification of various oils with methanol have been reported. Kim et al. [9] applied Na/NaOH/-Al2O3 as a strong base catalyst to the transesterification of soybean oil. They showed a comparable performance to the conventional homogeneous NaOH catalyst. Kawashima et al. [10] investigated the production of biodiesel using stirred reactor using heterogeneous base catalysts. Thirteen different kinds of metal oxides containing calcium, barium, magnesium, or lanthanum were prepared as catalysts. The authors concluded that, calcium-containing catalysts show high activities.

On the other hand, only a few or limited papers have investigated the use of reactive distillation columns. Arvinder et al. [11] developed reactive distillation technique to produce biodiesel from yellow mustard seed oil and use homogenous catalyst (KOH). The column was equipped with sieve-tray internals. The results showed that, the optimum process temperature was 65°C. From literature review, it is clear that, there are limited studies or investigations that use reactive distillation technique with heterogeneous solid catalysts. Therefore, the main purposes of this work are:

1-Study the ability of biodiesel production by using reactive distillation technology with the use of heterogeneous solid catalysts (Zeolites).

2-Examine the effect of catalyst modifications and reaction time on the transesterification reaction and test the catalysts activity and selectivity to desired product.

2. Experimental Work

2.1 Materials

Sunflower oil was used as a raw material for the production of biodiesel. This type of oil was filtered to remove impurities. A laboratory grade methanol (99.9 wt%) was purchased from Fluka. Two parent types of solid catalysts are used in present investigation: NaX zeolite, and Na5A zeolite (Landa Company). Other chemicals were used such as $MgCl_2$, and $CaCl_2$ analytical grade.

2.2 Catalyst Preparation

The catalysts were prepared by impregnation of original zeolite with aqueous solutions of the corresponding salt chloride. The salt chlorides applied to the study were $MgCl_2$, and $CaCl_2$. Therefore, each 40gm of zeolite was mixed for 1 hr with the salt solution (3N of $MgCl_2$, or 3N of $CaCl_2$). Then, the mixture was impregnated for 72 hrs to get the maximum ion exchange of sodium by corresponding (Mg or Ca) cations. It is important to mention here, that after 72 hrs of the exchanging time, the ion exchange reaction reached an equilibrium in which no further replacement occurs [12].

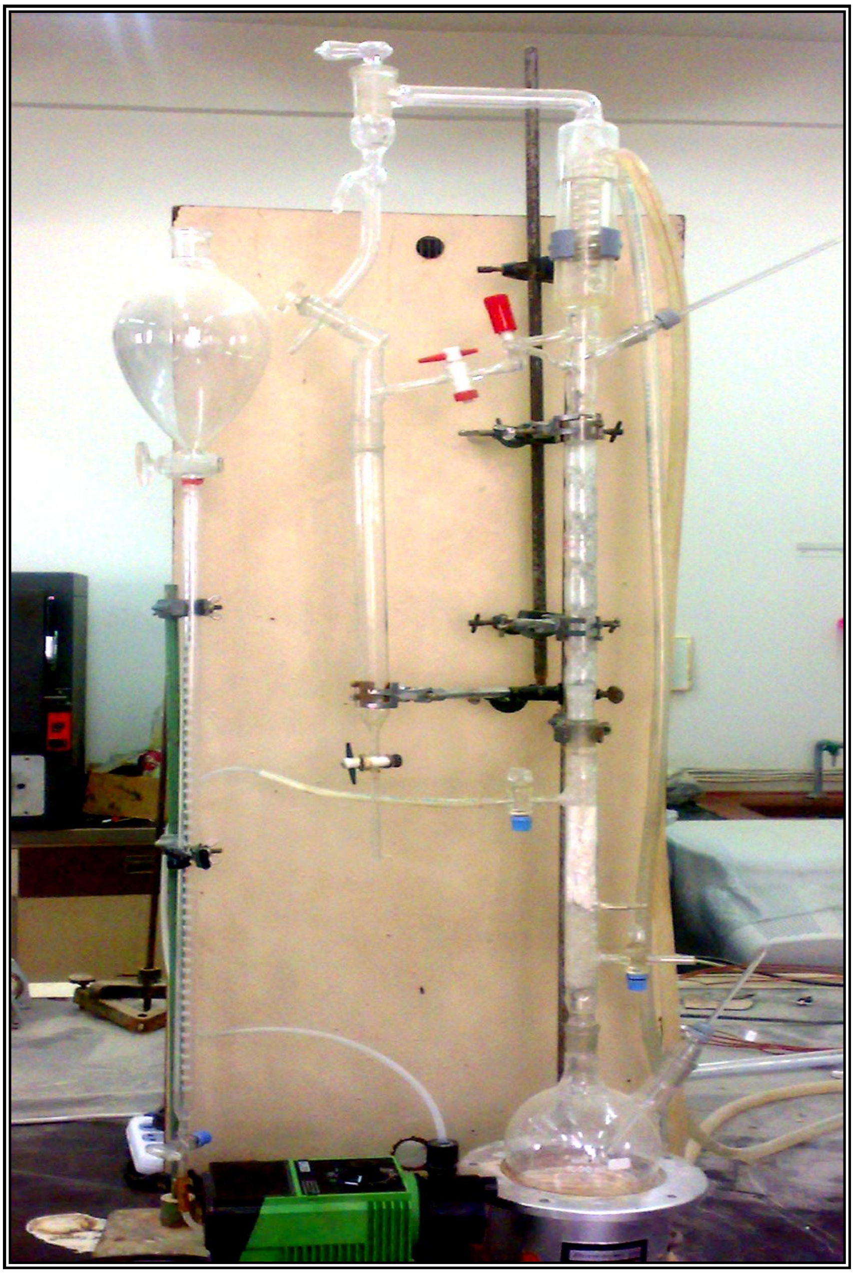
After impregnation process, each catalyst type was washed with dionized water, filtered, and then it was dried in an oven at 120 ◦C for 5 hrs. The dried sample then was calcined at 350 ◦C for 3 hrs before being used. Therefore, in the present investigation, six types of catalysts were used NaX, MgX, CaX, Na5A, Mg5A, and Ca5A.

2.3 Experimental Procedure

In the present work, the heterogeneously catalyzed transesterification of vegetable oil and methanol to methyl ester (biodiesel) in continuous reactive distillation column is studied. A view of the laboratory scale reactive distillation system is shown in Figures (1), while, Figure (2) shows a schematic diagram of the process.

The column has an inner diameter of 2.5 cm and is about 60 cm height divided into three sections as follows: the stripping section = 15 cm, reaction section=15 cm, and reactiving section = 30 cm. The rectifying and stripping sections were filled with rushing ring glass packing (non-reactive packing) of 6 mm height, and 4, 6 mm inner and outer diameter respectively. The voidage fraction of the column was about (0.7). The middle section of the column was filled with 20 gm of the catalyst. The top of the column was connected to a condenser where a coolant (water at temperature T= 20 ^{o}C) was circulated to condense vapor from the reactive distillation column.

Fig. (1) Experimental setup of laboratory scale packed reactive distillation column.



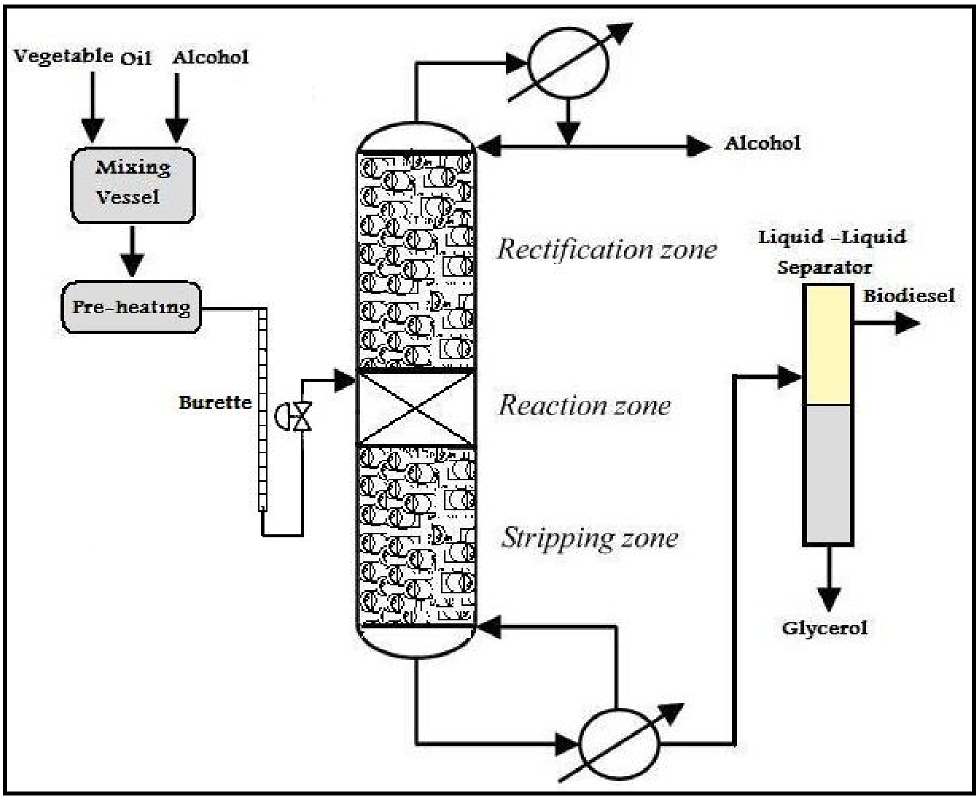


Fig. (2) Diagram of the experimental packed reactive distillation system.

The bottom of the column was connected to a reboiler (500 cm^3 three neck flask). Heat supply required for the reboiler was regulated by a variable transformer via adjustable voltage. The product mixture was withdrawn from the reboiler and sent to the separation column. Biodiesel/glycerol separation was carried out by gravity in a continuous liquid-liquid separator (gravity decanter) with feed-point at the middle of the separation column.

In the reactive distillation unit, methanol and oil were fed separately to mixing section (pre-heating section). The flow rate of feed mixture was controlled through metering burette. Then, the mixture was fed into the upper part of the catalytic section of the column continuously. As the feed mixture is introduced into the catalyst in the reactor, the reaction was started. All experiments were carried out at a constant reaction temperature of 65 ^{o}C , atmospheric pressure, methanol/oil ratio of 4, and total reflux ratio. The total reaction time was 60 min for each catalyst. The main process parameters examined in this study were: the performance of catalyst types, alcohol-to-oil ratio, and reaction time.

The chemical compositions of catalysts were analyzed by using gravimetric analysis methods. The specific surface areas of the catalysts were measured by nitrogen physisorption (BET). On the other hand, the products were analyzed using a Shimadzu GC-2014 gas chromatograph coupled with FID, using S.G.E. capillary column of 25m length and 0.22 mm inner diameter, .

3. Results and Discussion

3.1 Catalysts Characteristics

The design and operation of the reactive distillation is very difficult because of complicated transport processes (hydrodynamic, mass, and heat transfer) and reaction kinetics that occur in such type of unit [4]. Therefore, one needs to get a detailed understanding of the reaction mechanism, kinetic, and catalyst properties. Understanding of catalyst performance and reaction kinetic will enable the design of a new catalyst with high activity and selectivity for desired products.

Table (1) shows the chemical composition of the parent catalysts (NaX and Na5A) and their physical properties and chracterization. From the results of this table it is clear that, the total surface area of NaX catalyst (330 m^2/g) is higher than that of Na5A catalyst (85 m^2/g). For this reason NaX-type zeolie has found a wide range of applications in industry as a catalyst rather than Na5A type [12].

Table (1) The characterization and chemical composition of parent zeolites.

Property	NaX-Zeolite	Na5A-Zeolite
SiO_2/Al_2O_3	2.5	1.6
SiO_2	44.2	38.0
Al_2O_3	20.4	30.0
Na_2O	13.1	12.9
Loss on Ignition	19.0	16.5
Total Surface Area (m^2/g)	330	85
Total Na^+ Exchange By Metal Cation %	85% by Mg 81% by Ca	78% by Mg 72% by Ca
General Shape	Extrudates 3mm x 5mm	Extrudates 3mm x 5mm

3.2 Catalysts Performance

It is important to mention here that, in the present work, design of experiments has been applied to optimize the catalyst type that is used in the synthesis process of methyl esters. Therefore, all experiments were carried out at a constant reaction temperature of 65^{o}C and 60 min of the reaction time. This temperature represented the optimum temperature for the transesterfication reaction [1, 4, 10]. On the other hand, such temperature is representing the boiling point of methanol (64.6°C) that was recovered from the top of reactive distillation. Conversely, the percentages of conversion of reaction mixture into methyl ester (biodiesel) forms were determined by GC. The first group of peaks is methyl esters followed by mono, di and triglycerides.

The effect of reaction time on the conversion of sunflower oil to biodiesel was studied by using different catalyst types (NaX, MgX, CaX, Na5A, Mg5A, and Ca5A). Figure (3) shows the effect of catalyst type on the percentage conversion to biodiesel as a function to reaction time for X-zeolite catalysts. From this figure, it is clear that, the CaX catalyst is the most suitable catalyst for the heterogeneously catalyzed transesterification of sunflower oil with methanol to produce biodiesel. The modified CaX catalyst gives the highest final conversion to biodiesel of ~92% than that of the MgX and parent catalyst (NaX) of 69% and 56% respectively. Therefore, it can be concluded that, the catalyst type and modification process were found to have the most significant influence on conversion to biodiesel.

Usually, the transestefication reaction to biodiesel is combined with side reaction that is the saponification reaction [3, 5]. This side reaction is promoted to reduce the conversion to biodiese and the separation and purification of the final biodiesel will be more difficult. Then, it is concluded that, during the operation with reactive distillation system, there exists no saponification reaction (no side reaction). Therefore, the CaX catalyst could give a faster reaction rate without a drop in the conversion.

It is important to mention here that; the production of biodiesel by using reactive distillation technology with solid catalysts (Heterogeneous mode of operation) is implemented in this study successfully. The use of heterogeneous catalysts in reactive distillation will be integrated reaction and separation into the same unit, thus intensifying the mass transfer while simplifying the process operation.

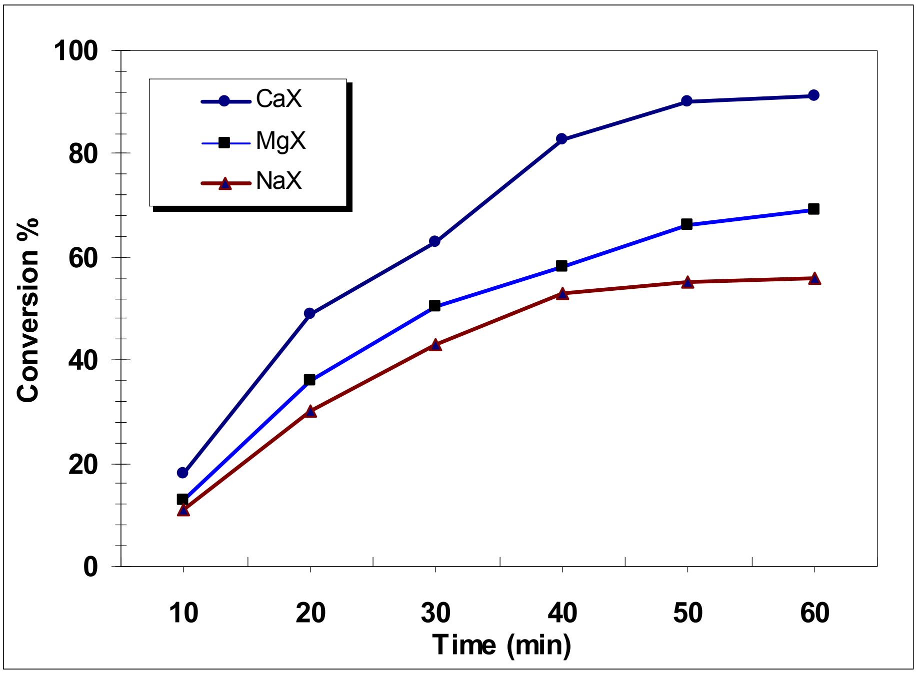


Fig. (3) The effect of catalyst type (NaX, MgX, and CaX) on the percentage conversion to biodiesel.

On the other hand, Figure (4) shows the effect of catalyst types (Na5A, Mg5A, and Ca5A) on the percentage conversion to biodiesel. It is clear that, the calcium type catalyst (Ca5A) also gives the highest conversion level (~ 48%) in comparison with the other two types of catalysts Mg5A, and Na5A of 34% and 31% respectively.

From the comparison of the results of Figures (3) and (4), it can be concluded that, the X type catalysts reach higher values of final conversion than Na5A catalysts at 60 min of reaction time. This behaviour is regarded be due to the higher surface area of X-type catalysts than that of 5A-type [12]. Also, from the two figures, the transesterfication reaction starts lineally with reaction time, then, all curves show horizontal behaiour at the final reaction time of 60 min. This indicates that, the transesterification reaction is in the equilibrium state and there is no further increase in the percentage conversion achieved.

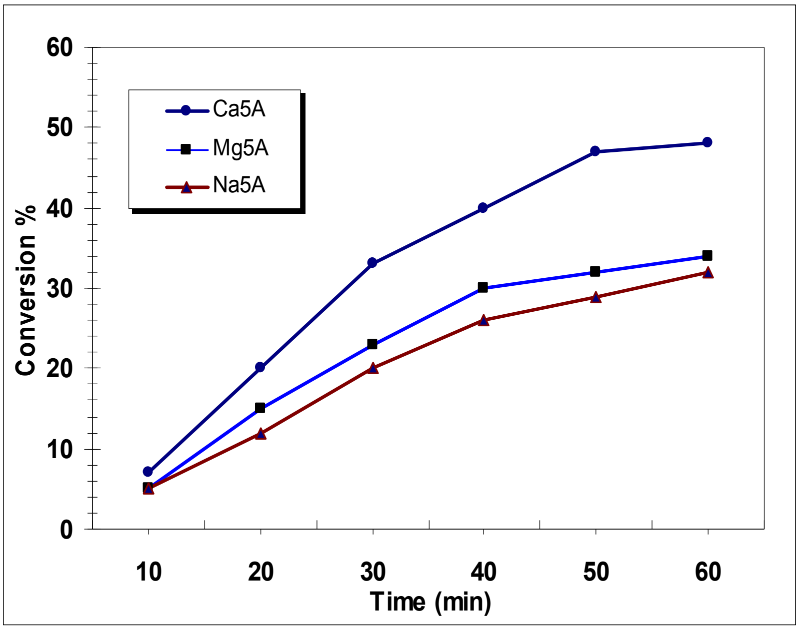


Fig. (4) The effect of catalyst type (Na5A, Mg5A, and Ca5A) on the percentage conversion to biodiesel.

It is generally known that, in early stage of the transesterification, the reaction is limited by the mass transfer of alcohol to vegetable oil phase. As the reaction progresses, the formation of esters improves the solubility of alcohol in the oil phase, and the reaction rate is then governed by kinetics. In the third stage, the reaction reaches its dynamic equilibrium of conversion, which is primarily dependent on the alcohol-to-triglycerides molar ratio. Therefore, to avoid the undesirable reaction, it can be found the use of heterogeneous solid catalysts in reactive distillation column is dominated. Such explanation is in accord with the work of Arvinder et al. [10].

3.3 Prepared Biodiesel Specifications

In this section of the work, it is focuses on the results of CaX catalysts. The biodiesel fuel properties such as: density, viscosity, flash point, cloud point, pour point, and water content were determined and are reported in Table (2). The physical fuel properties of produced biodiesel in general are comparable to those of recommended standard diesel [13] and to those were prepared by different investigators in literature [2, 4, and 8]. The results show that the properties of the prepared biodiesel are in agreement with standard and the literature values.

Density can be easily measured at the time of manufacture, using a simple hydrometer method [4]. Therefore, Table (2) indicates that, the prepared biodiesel has higher density than mineral diesel. The denser biodiesel will characteristically sink to the bottom of the tank and this can lower fuel consumption which is determined volumetrically; so the denser the fuel, the higher the consumption will be.

Physical Properties	Standard Diesel [13]	Biodiesel Prepared by using RD technology	Literature values [2, 4, 5, and 8]
Density (g/cm^3) at 15.6 °C	0.85	0.87	0.86 - 0.90
Kinematic Viscosity (c.St) at 40 °C	~ 3	4.2	3 - 5
Flash Point (°C)	70	103	100 - 120
Fire Point (°C)	105	120	90 - 130
Pour Point (°C)	-9	4	-2 to +10
Water Content (mg/kg)	250	300	200 - 500
Sulfur Content wt%	~ <1	~ 0.0	~ 0.0
Carbon Residue wt%	1.5	0.81	0.4 - 1.0
Cetane Number	53	60	55 - 62

Table (2) The physical properties of the standard diesel and prepared biodiesel by using reactive distillation wih CaX catalyst.

Also, from Table (2) it can be concluded that, the viscosity of biodiesel is higher than that of mineral diesel which can lead to problems in fuel delivery systems [2, 13]. High viscosity can lead to poor combustion which leads to coking of injector tips and engine power loss. Viscosity decreases with unsaturation but increases with the presence of mono, di or triglycerides. Lower viscosity can also indicate the presence of methanol in the biodiesel, which can be confirmed by measuring flash point (the lower the flash point, the more methanol is present).

In the present work, the water content of the methyl ester was less than 0.03% (300 mg/kg). Water in the sample can promote microbial growth, lead to tank corrosion, participate in the formation of emulsions, as well as cause hydrolysis or hydrolytic oxidation. This result is in agreement with work of Arvinder et al. [10] and Kawashima et al. [11]. On the other hand, the stability of biodiesel depends on the feedstock used for the biodiesel production. The feedstock with larger proportion of saturated fatty acids will be more stable than those having larger proportion of unsaturated fatty acids. But, higher portion of saturated fatty acid lowers the low temperature properties such as cloud and pour points [8].

3.4. Effect of Methanol/Oil Molar Ratio

The CaX type catalyst was selected to study the effect of methanol/oil ratio on the total conversion to biodiesel (methyl ester). The experiment was done at different methanol/oil molar ratio ranging between 1:1, 2:1, 3:1, and 4:1 and with constant weight of catalyst of 20 g. Figure (5) shows the effect of methanol/oil ratio on biodiesel content. As illustrated in this figure, with increasing the methanol/oil ratio from 2 to 4, the biodiesel content is increased. At the ratio of 4, the highest biodiesel content of 94 is attained. There is no significant improvement in the biodiesel formation with a further increase in the ratio to 6.

From results of Figure (5), it can be seen that the transesterification reaction uses a relatively large amount of methanol. This increased methanol requirement could be explained on the basis that the zeolite catalysts exhibits a real heterogeneous catalysis in which the mass transfer between the immiscible liquid phases and the solid catalyst surface is a major limitation. The larger amount of methanol would then facilitate the diffusion of reactants and the formation of active methoxide species, resulting in higher methyl ester content. Such explanation is in agreement with the work of Marchetti et al. [2] and with the basic mass transfer operation in zeolites [12].

Therefore, it can be concluded that, because of the presence of an equilibrium reaction a higher amount of alcohol should be used so that the reaction will be towards the desirable product. This conclusion is in agreement with the work of Khalid et al. [4] and Kim et al. [9].

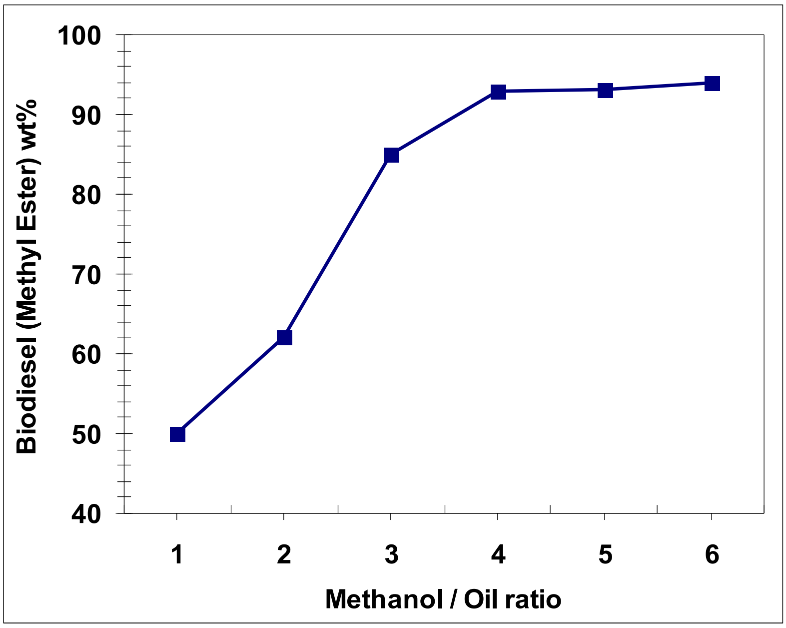


Fig. (5) Effect of Methanol/Oil ratio on the methyl ester (biodiesel) in product using CaX catalyst.

4. Conclusions:

1- In this study, the reactive distillation technique to produce biodiesel is implemented successfully by using heterogeneous solid catalysts.

2- It was concluded that, the modified catalyst type CaX is a suitable alternative to perform the transesterification reaction with good results and has better final conversion than other types.

3- The catalytic distillation column performance is evaluated by running the column at different operating conditions. The operating parameters including type of catalyst, total feed flow rate, and molar ratio of methanol to oil are very important to determine the performance of reactive distillation.

4- In comparison with homogenous catalysts, high conversion rates to biodiesel are obtained by using reactive distillation technique with solid catalysts because it is known that, when reversible reaction is conducted, then the equilibrium will prevent high conversions. Therefore, the reactive distillation technique can be employed to remove the reaction products from the reaction zone to improve overall conversion rate and selectivity.

5-Some important physical and fuel properties of the resultant biodiesel products meet the standards for diesel fuel and biodiesel.

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الخلاصة

في هذا البحث تم اختبار عملية انتاج وقود الديزل الحيوي باستخدام تقنية التقطير ذو المفاعل (Reactive Distillation) . حيث تم استخدام نوعين رئيسين من العوامل المساعدة هما زيولات NaX وزيولايت Na5A في تفاعل Transesterification للميثانول وزيت عباد الشمس. وخلال العمل تم تطوير أنواع الزيولات باستخدام طريقة التبادل الآيوني للصوديوم بكاتيونات الكالسيوم والمغنيسيوم للحصول على انواع مطورة من العوامل المساعدة.

تم تصنيع المنظومة المختبرية الخاصة بالتفاعل من الزجاج المقاوم للحرارة وبقطر داخلي 2.5 cm للبرج وبارتفاع 60 cm موزعة على النحو التالي:

stripping zone=15cm reaction zone=15cm, and rectification zone=30 cm.

م حشو منطقة التفاعل بالعامل المساعد والمنطقتين الاخريين بحشوا زجاجية نوع rushing ring بابعاد

6 mm ارتفاع الحشوة الواحدة وقطر داخلي وخارجي 4 mm و 6 mm على التوالي.

تم دراسة تاثير نوع العامل المساعد على نسبة التحول الكلي، حيث تم اجراء جميع التجارب العملية من خلال اختبار العوامل المساعدة بدرجة حرارة تفاعل ثابتة هي 65 ^{o}C وضغط جوي وبنسبة راجع كلية. حيث اظهرت النتائج انه يمكن انتاج وقود الديزل الحيوي باستخدام تقنية التقطير ذو المفاعل وبنجاح وباستخدام عوامل مساعدة صلبة.

اعتماداً على الأنواع الست من العوامل المساعدة المستخدمة في البحث، تم الإستنتاج ان العامل المساعد نوع CaX هو الأكثر ملائمة لإجراء تفاعل Transesterification لإنتاج الوقود الحيوي وبنسبة تحول كلية تقترب من 92% اذا ماقورنت مع الأنواع الأخرى.

وخلال الدراسة تم الإستنتاج ان نسبة الكحول الى الزيت المثلى الخاصة بالتفاعل هي 4 والتي أعطت أعلى نسبة تحول الى الديزل الحيوي تقرب من 94% . من ناحية أخرى فان الخواص الفيزيائية لوقود الديزل الحيوي المنتج بهذه الطريقة الحديثة تنطبق وبشكل جيد مع مواصفات وخواص وقود الديزل.