

Biodiesel production from sunflower oil using K_2CO_3 impregnated kaolin novel solid base catalyst

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Abstract

Kaolin clay material was loaded with potassium carbonate by impregnation method as a novel effective and economical heterogeneous catalyst for biodiesel production of sunflower oil via the transesterification reaction. The structural and chemical properties of the produced catalysts were analyzed by several characterization tests including the BET-BJH, XRD, SEM and FTIR. Influence of the K_2CO_3 impregnation level was examined by comparing the catalytic activity of different produced catalysts. To expand the efficiency of transesterification reaction, parameters of reaction were optimized including; the molar ratio between methanol and oil, concentration of catalyst, and duration of the reaction. The highest yield of biodiesel over the K_2CO_3 /kaolin catalyst was around $95.3 \pm 1.2\%$. It was achieved using kaolin supports impregnated with 20 wt.% of K_2CO_3 . The optimum reaction conditions were found to be catalyst reactor loading of 5 wt.%, reaction temperature of 65 °C, methanol: oil molar ratio of 6:1 and reaction duration time of 4 h.

Keywords: Transesterification, Solid base Catalyst, Sunflower Oil, Kaolin, Potassium Carbonate.

1. Introduction

The progress and development through industry and life of human beings worldwide have led the fossil fuels to become the primary source of the energy. With increasing the usage of this source, new concerns have manifested. Though still some apprehensions such as, irreplaceable sources of fossil fuels or global warming exist [1]. In other words, the global warming is one of the most significant concerns in the world. The main reason for this problem is that, the utilization of the fossil fuels is growing which in turn leads to CO₂ production as a greenhouse gas. Thus, such fuels ought be substituted with others which impose much less damage to the environment.[2]. One such alternative which is commonly used by many countries, is the Biodiesel fuel possessing combustion properties very similar to the fossil fuels. This has attracted massive attentions of the researchers around the world.

Biodiesel is defined as the mono-alkyl esters of vegetable oils or animal fats. Diesel fuel can also be replaced by Biodiesel made from vegetable oils. Biodiesel consists of a short chain of fatty acid methyl esters (FAME), which come from fat and vegetable oils. Biodiesel commonly produced in two types of reactions. These two are transesterification or esterification reactions of triglycerides and free fatty acids (FFA) in the presence of an alcohol in particular; methanol. Amongst all these procedures, the most usual and popular one catalyzes the transesterification process of triglycerides for two main reasons; the first advantage is high efficiency and yield of the reaction hence; no need

for advanced systems or complicated aspects and the second one is being economically appropriate. Biodiesel production reaction is performed slowly, so in order to increase the reaction rate, one has to use an appropriate catalyst. On the other hand, different catalysts with different properties which provide several options to produce Biodiesel have been already introduced. All these methods' raw material comes from vegetable oils or animal fat, and this is one of the Biodiesel's advantages which makes biodiesel renewable as well as with less pollution [3].

Heterogeneous and homogeneous catalysts can both used to increase efficiency of the biodiesel production through the transesterification reaction. Homogeneous basic catalysts like KOH and NaOH are the essentially used materials for this objective. Although these species have a number of benefits like their higher catalytic activity in lower reaction duration and moderate reaction conditions. Their utilization is bringing up a number of serious problems, such as difficulty for separating catalyst from product as well as a sensitivity to FFA of feedstock and water. H_2SO_4 , HCl and other homogeneous acid catalysts are also had several issues including; requiring long reaction time, high reaction temperature and more difficult to be separated from the reaction mixture to be recycled. To avoid these issues, the main focus attracted to the heterogeneous catalysts that can be reused, have less vulnerability towards FFA and water, and more friendly to the environment [4]. Until this point, various basic solid catalysts, like single metal oxides, such as CaO [5] and MgO [6] have been utilized for biodiesel production of vegetable oils. Also, mixed metal oxides have been utilized to enhance the basic strengths of the catalysts. CaTiO_3 , CaMnO_3 , $\text{Ca}_2\text{Fe}_2\text{O}_5$, CaZrO_3 and CaO-CeO_2 [7] catalysts are some instances of solid catalysts showing high basicity and reusability for biodiesel production.

In order to enhancement the basicity of catalysts, impregnation of some catalytically active materials such as potassium or sodium was recommended. Talc [1], sepiolite [8] and Al_2O_3 [4]

were altered with basic catalytically active materials and utilized as effective heterogeneous basic catalysts for the biodiesel production. The catalytic activities of sodium or potassium species impregnated into catalyst supports relied on the kind of the utilized precursor, the potassium or sodium impregnation amount and the preparing variables.

Recently, investigations on the utilizing of clay materials such as palygorskite, sepiolite, bentonite, talc and kaolin as a support of catalysts for biodiesel production were highly recommended due to the high thermal stability, inexpensive materials and abundant in nature [1]. Kaolin is obtained from mineral Kaolinite, and it is a hydrous aluminum silicate by $\text{Al}_2\text{SiO}_5(\text{OH})_4$ chemical formula. Kaolinite clay used in the ceramic industry, paper industry (as filler), petroleum industry, agriculture, etc. Kaolin's chemical structure does not change and does not expand when it is contacted with water. it is a cheap and adaptable raw material for the catalyst base [9]. Clay is an earthy, soft and loose material containing particles with the grain size. Most of the mineral material in their purest state is white and also in this case, the clay is white. Lately, this research team focused on heterogeneous catalysts' development by using clays. In this case, the biodiesel production of CaO/Talc, [10] and K_2CO_3 /Talc [1] catalysts from the transesterification reaction of canola and sunflower oils was published.

Here, the K_2CO_3 loaded (10, 20 and 30 wt.%) kaolin were prepared as a new catalyst and used for the biodiesel production via transesterification reaction of sunflower oil with methanol. In addition, impacts of reaction variables including; catalyst loading into the reactor, reaction duration time and molar ratio between methanol and oil on the catalytic activity of the prepared catalysts for biodiesel production were studied. Ultimately, stability and reusability of the prepared catalysts were undertaken for the biodiesel production via transesterification reaction.

2. Experimental

2.1. Materials

Kaolin powder ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) was purchased from the Merck. Sunflower oil was obtained from a local market (Tehran, Iran). The physical and chemical properties of sunflower oil are summarized in Table 1 and fatty acid composition of sunflower oil is presented in Table 2. Methanol (99% of purity) and Potassium carbonate (K_2CO_3) were both purchased from the Merck.

2.2. Catalyst preparation and procedure

Three kaolin-based catalysts with various K_2CO_3 loading levels (10, 20 and, 30 wt.%) were synthesized by the wet impregnation method. The aqueous K_2CO_3 solution was dissolved in deionized water and then gradually added to kaolin powder. The resulting mixture was then continuously stirred at 70 °C for 5 h. Eventually, the precipitate was collected, dried at 120 °C for 24 h and subsequently calcined at 550 °C under the atmospheric pressure for 3 h.

2.3. Methods for characterization

The crystallography of the produced samples was identified by powder X-ray diffraction (XRD). The analysis was carried out using a Rigaku RU2000 rotating anode powder diffractometer (Woodlands, TX). Specific surface area measurements and mean pore diameters of catalysts were evaluated by the BET test by using Quantachrome Autosorb 1 MP according to the BET-BJH method. Before measuring specific surface area, the samples were dried in a furnace at 120 °C for 24 h. [1, 11, 12]. In order to analyze surface functional groups Thermo Avatar spectrometer, identified the Fourier transform infrared (FTIR) of the powders in wave number range of 400 – 4000 cm^{-1} using KBr pellet. Hammett indicators were used to evaluate the basic property of the

produced samples. The indicators for Hammett method contained 4-nitroaniline ($H_a=18.4$), 2,4-dinitroaniline ($H_a=15.0$), phenolphthalein ($H_a=9.8$) and bromothymol blue ($H_a=7.2$). The produced samples' basicity were determined by using the benzene carboxylic acid indicator and titration until the color changed back to the original color of samples [1, 11, 12].

2.4. Transesterification reaction procedure

The transesterification reaction of sunflower oil for biodiesel production, was performed in a three-necked round glass bottom batch reactor with capacity of 100 mL equipped with a water-cooled condenser for cooling methanol, magnetic stirrer, sample port and thermometer. At first, to activate the catalyst, a proper amount of the catalyst was stirred with methanol and warmed up to 40 °C for 30 min. Thereafter, sunflower oil was added into the flask and the reaction mixture was stirred for 4 h at 65 °C. After the completion of reaction, the catalyst was separated from the reaction mixture by filtration through a filter paper. Nevertheless, the product mixture was kept isolation in decanter for 24 hours. The top layer contained biodiesel and the bottom layer contained glycerol due to different densities of 0.86 and 1.126 g/cm³. The excess methanol was eliminated by vaporizing the biodiesel at 65 °C. The samples were mitigated by n-hexane and then measured by a gas chromatograph (GC) for evaluating the fatty acid methyl ester (FAME) yield.

Biodiesel yield was evaluated by a PerkinElmer Clarus 580 gas chromatograph (GC) with a flame ionization detector (FID) and SUPRAWAX-280 column. Helium was utilized as a carrier gas at a split ratio of 100:1. Injector and detector temperatures were set at 280 °C. The oven temperature was started at 60 °C for 2 min, then increased to 200 °C at a rate of 10 °C.min⁻¹, and 240 °C at a rate of 5 °C.min⁻¹ and maintained at this temperature for 7 min. The internal standard, methyl nonadecanoate was prepared to assess the yield of methyl ester.

The methyl ester yield was calculated with the following equation:

$$Yield(\%) = \frac{\text{weight of biodiesel} \times \%FAME}{\text{weight of sunflower oil}} \times 100\% \quad (1)$$

Where %FAME is the concentration of fatty acid methyl ester that was obtained by the GC analysis through the following equation:

$$FAME(\%) = \frac{\sum A - A_S}{A_S} \times \frac{C_S V_S}{m} \times 100\% \quad (2)$$

Where m , $\sum A$, A_S , V_S and C_S were used mass of the sample, total peak area of the methyl esters (C_{14} - $C_{24:1}$ in specific), peak area of the methyl nonadecanoate, volume of methyl nonadecanoate used in solution (mL) and solution concentration of the methyl nonadecanoate (mg/mL) [1, 13].

2.5. Stability test

To investigate the stability of the produced catalyst, the transesterification reaction was operated under optimum reaction condition (5 wt.% of catalyst amount into the reactor, methanol: oil molar ratio of 6:1, reaction temperature of 65 °C, reaction duration time of 4 h) for five successive times. Catalyst was filtered from the reaction's products by centrifugation and recovered after each cycle. In order to recover the utilized catalyst, it was washed by methanol to eliminate the adsorbed organic species from the catalyst's surface. The resulting catalyst was then dried at 100 °C for 24 h. Eventually catalyst recalcined at 550 °C for 3 h and then reutilized for the next reaction run.

3. Results and discussion

3.1. Catalyst characterization

for the examination of the impacts of the K_2CO_3 loading, three catalysts were prepared through the same method of impregnation described in the previous sections with various loadings of K_2CO_3 (10, 20, and 30 wt.%). In Fig 1, XRD diagram of the pure kaolin and K_2CO_3 /kaolin catalysts with various K_2CO_3 loadings are shown. The peaks at $2\theta = 20.1^\circ, 21.1^\circ, 28.8^\circ, 32.1^\circ, 35.8^\circ, 38.6^\circ, 45.5^\circ, 50.9^\circ$ and 70.1° were determined to the kaolin structure (JCPDS file (00-0002-0105)). The characteristic peaks of K_2CO_3 were perceived at $2\theta = 13.2^\circ, 27.4^\circ, 30.2^\circ, 31.1^\circ, 33.2^\circ, 35.6^\circ, 39.0^\circ, 41.8^\circ, 43.8^\circ, 45.6^\circ, 51.8^\circ, 54.1^\circ, 57.8^\circ$ and 69.9° (JCPDS file (00-001-1001)). In the K_2CO_3 impregnated catalysts, the characteristic bands of kaolin were recognized, representing the way that kaolin protects its structure from K_2CO_3 loading. Furthermore, the peaks at $2\theta = 34.7^\circ, 37.7^\circ, 42.6^\circ$ and $2\theta = 32.2^\circ, 32.7^\circ$ and 40.0° were credited to the K_2O (JCPDS document (00-027-0431)) and Al—O—K (JCPDS document (96-210-5201)) species. The intensities of Al—O—K and K_2O peaks were improved upon the increasing of the K_2CO_3 loading. Stuningly, no peaks of K_2CO_3 were appeared in the XRD patterns of the prepared catalysts. This was totally according to decomposition of K_2CO_3 .

Structural and chemical characteristics of the produced catalysts and pure kaolin were shown in Table 3. As arranged, the specific surface area of pure kaolin was $11.5 \text{ m}^2/\text{g}$. After K_2CO_3 loading on kaolin, this worth has been decreased. Additionally, it may be deduced that the K_2CO_3 loading increasing causes the decreasing of the specific surface area of the kaolin support. This examination was ascribed to the K_2CO_3 species covering the surface of the kaolin.

In Fig 2, the adsorption-desorption isotherms of the pure kaolin and K_2CO_3 /kaolin prepared catalysts are represented. As demonstrated all isotherms indicated type II of the IUPAC details. Fig 3, has shown the BJH diagram which achieved from pure kaolin and produced catalysts. It's shown that the pure kaolin and K_2CO_3 /kaolin prepared catalysts presented alike pore size

dispersions. Calculations of the average pore diameters of the pure kaolin and prepared catalysts illustrated in Table 3. It indicated that by the loading of the K_2CO_3 , average pore diameter was decreased. Triglyceride and glycerin molecules' dimensions as stated by researcher, were respectively ~ 2.5 and 0.6 nm [1, 11]. The comparison of the average pore diameter of the prepared catalyst with the dimensions of the triglyceride molecules proposes that the triglyceride species can easily penetrate into the pores of the prepared catalyst.

The Hammett indicator method has been used for the basicity of the pure kaolin and K_2CO_3 /kaolin prepared catalysts. As appeared in Table 3, the pure kaolin demonstrated the most minimal basic strength ($H_{\leq} \leq 7.2$) and the basicity of 0.18 mmol/g. Notwithstanding, by loading with K_2CO_3 , the basic strength of the produced catalysts expanded altogether. It is critical to specify that, among K_2CO_3 impregnated catalysts, the basicity estimations of the produced catalysts with 20 and 30 wt.% of K_2CO_3 loading level were astoundingly greater than catalyst with 10 wt.% of K_2CO_3 loadings.

In this section, Fig 4 presented the SEM image of $K_2CO_3(20\%)/kaolin$ catalyst. The crude kaolin principally comprises of impregnation of flaky particles with rough surface. These attributes are the characteristic morphological traits of high crystalline kaolin. After the impregnation of $K_2CO_3(20\%)$ on kaolin (Fig 4), K_2CO_3 particles have covered part of the kaolin pores and decrease the diameter of these pores. Nonetheless, this impregnation actuated a few conglomerations where the sheets of kaolin get to be more packed. The decreased mean pore diameters which being

classified in Table 3 would be validated by this morphology where also, each pore diameter reduction lead to a biodiesel fuel yield improvement [14, 15].

The FTIR spectra of the kaolin, K_2CO_3 , and then $K_2CO_3(20\%)/kaolin$ catalyst are shown in Fig 5. Kaolin related bands are perceived at 3672.1 cm^{-1} was related to the hydroxyl stretching vibration, 1057.9 cm^{-1} was corresponded to Si-O-Si stretching, and the bands at 479.1 and 540.5 cm^{-1} was attributed to Si-O, and Al-O stretching [16]. Furthermore, the related bands of K_2CO_3 were perceived at 3192.9 , 1448.9 , and 1379.9 cm^{-1} . It was notable that no peaks of K_2CO_3 were observed in the FTIR range of the $K_2CO_3(20\%)/kaolin$ catalyst which proposed that the K_2CO_3 was totally decomposed or reacted with the support, and the new phases of Al—O—K and K_2O , was appeared and this issue was also confirmed by the XRD analysis presented above.

3.2. Catalytic activity tests

Impact of the K_2CO_3 loading level on the activity of the catalysts for the biodiesel production are illustrated in Fig 6. Biodiesel production via transesterification reaction was operated by using a 5 wt.% of K_2CO_3 (20%)/kaolin catalyst amount into the reactor, methanol: oil molar ratio of 6:1, at a reaction temperature of $65\text{ }^\circ\text{C}$ for 4 h of reaction duration time. The methyl ester yield shows an increase from 7.1% to 95.3% when the K_2CO_3 impregnation level was increased from 0-20 wt.%, but then it decreased to 94.9% after addition of K_2CO_3 to 30 wt.%. According to Table 3, a strong correlation exists between the basicity value of the prepared catalysts and their activity, which the K_2CO_3 loading level lower than 20 wt.% did not supply enough active site upon surface

of the catalysts for the biodiesel production according to its lower basicity. However, when the K_2CO_3 loading level was above 20 wt.%, the addition of 30 wt.% K_2CO_3 had disturbing influence to the active sites and there was poor K_2CO_3 distribution in the catalyst, which resulted partial dissolution of the support [1, 8, 17]. The highest yield of methyl ester was observed at a higher basicity of 1.85 mmol/g

The impact of the $K_2CO_3(20\%)/kaolin$ catalyst amount into the reaction on the yield of methyl ester was appeared in Fig 7. The reaction was operated under optimum conditions (methanol: oil molar ratio of 6:1, reaction temperature of $65^\circ C$ and reaction duration time of 4h). The yield of methyl ester gradually increased when the catalyst loading amount into the reactor increased from 2 to 5 wt.%. Nonetheless, there was observed a slight decreasing in the biodiesel yield when 7 wt.% was applied, which exhibited that though an adequate amount of catalyst was needed for the optimum yield, and the excess amount of catalyst did not increase the biodiesel yield. This was because an excessive amount of catalyst might make the reaction mixture more viscous and there was more than enough mass transfer rate between the reaction media [1, 17, 18].

Another effective variable in ensuring a complete reaction that involves the biodiesel yield, is the molar ratio between oil and methanol utilized. In this section, methanol: oil molar ratio was used in various ranging from 3:1 to 12:1, and the reaction was operated under optimum conditions (K_2CO_3 (20%)/kaolin catalyst amount of 5 wt.% into the reactor, reaction temperature of $65^\circ C$ and reaction duration time of 4h). The results are shown in Table 4. As Shown, with the increase in methanol: oil molar ratio to 6:1, the biodiesel yield reached the highest value of $95.3 \pm 1.2\%$. This examination may be according to the reversible mechanism of the transesterification reaction. By

using an excessive amount of methanol: Oil molar ratio may improve the transesterification reaction equilibrium to the right side to yield more biodiesel [1, 19]. Further increase in methanol: Oil molar ratio more than 6:1 caused methyl ester yield to decrease. This may be according to the solubility of glycerol in methyl ester that leads to decrease in biodiesel yield [1, 20].

Under optimum conditions (K_2CO_3 (20%)/kaolin catalyst amount of 5 wt.% into the reactor, methanol: Oil molar ratio of 6:1 and reaction temperature of 65°C) the reaction duration time was investigated and the results have been illustrated in Fig 8. Various reaction duration times from 1 to 4 h were investigated. The yield of methyl ester was increased with extending the reaction duration time and the highest biodiesel yield of $95.3 \pm 1.2\%$ observed at 4 h of reaction time.

The physical and chemical properties of the produced biodiesel from sunflower oil an optimal conditions K_2CO_3 (20%)/kaolin catalyst utilizing were presented in Table 5. The most physical and chemical properties of the produced biodiesel at the optimal reaction conditions were within the prescribed ASTM D6751 and EN 14214 standards.

3.3. Reusability of the catalyst

It was observed through Fig 9 that, methyl ester yield of 95.3 to 85.2% were achieved for the first five cycles of transesterification of the sunflower oil using a K_2CO_3 (20%)/kaolin catalyst. In this section the reusability test was operated under optimum reaction condition (methanol: Oil

molar ratio of 6:1, 5 wt.% amount of catalyst into the reactor, reaction temperature of 65°C and reaction duration time of 4 h). Indicating that the catalyst could be recoverable at least 5 cycles with a 10% methyl ester yield drop from the 95.3% methyl ester yield achieved from fresh catalyst. The decay in methyl ester yield after each run might be attributed to the partial leaching of potassium into the reaction mixture during the consecutive runs and deposition of unreacted oil, glycerol or methyl ester on the active sites present on the surface of the catalyst [1, 11, 17].

4. Conclusions

In the present study, novel heterogeneous catalysts were successfully synthesized from raw kaolin clay materials that are loaded by various amount of K_2CO_3 species and utilized for the biodiesel production via the transesterification reaction of sunflower oil with methanol. Under the optimum conditions of catalyst producing and reaction variables (methanol: Oil molar ratio of 6:1, 5 wt.% of catalyst amount into the reactor, reaction temperature of 65°C and reaction duration time of 4 h), the $K_2CO_3(20\%)/kaolin$ catalyst (K_2CO_3 impregnation level of 20 wt.% upon the kaolin) achieved the maximum catalytic activity of $95.3 \pm 1.2\%$ according to its highest basicity. The results also exhibited that, after five cycles, the catalyst still achieve an acceptable methyl ester yield of $85.2 \pm 0.8\%$ and it was a reusable material for the transesterification reaction. Thus, the prepared $K_2CO_3(20\%)/kaolin$ catalyst was found to be a sustainable and promising novel catalyst for the biodiesel production of sunflower oil with methanol.

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Tables.

Table 1: The physicochemical properties of sunflower oil

Property	Unit	Value	Test method
Relative density at 20 °C	kg/m ³	918.8	ASTM D 4052
Kinematic viscosity at 40 °C	mm ² /s	33.5	ASTM D 445
Acid value	mg KOH/g	0.32	EN 14104
Water content	wt.%	0.1	ASTM D 1123
Flash point	°C	314.0	ASTM D 93

Table 2: Fatty acid composition of sunflower oil

Fatty acid	Structure	Composition (wt.%)
Palmitic acid	C 16:0	5
Stearic acid	C 18:0	4
Oleic acid	C 18:1	29
Linoleic acid	C 18:2	61
Other		1

Table 3: Structural and chemical properties of the kaolin and K₂CO₃/kaolin catalyst with various K₂CO₃ loading levels

Run	Chemical composition	BET surface area (m ² /g)	Average pore diameter (nm)	Basic strength (H ₋)	Basicity (mmol/g) [With Standard error ± 0.05]	Biodiesel yield (%)
1	kaolin	11.5	22.5	H ₋ < 7.2	0.18	7.1 ± 1.3
2	K ₂ CO ₃ (10%)/kaolin	8.9	16.9	7.2 < H ₋ < 9.8	1.04	78.2 ± 0.8
3	K ₂ CO ₃ (20%)/kaolin	6.5	14.1	9.8 < H ₋ < 15	1.85	95.3 ± 1.2
4	K ₂ CO ₃ (30%)/kaolin	6.4	13.9	9.8 < H ₋ < 15	1.83	94.9 ± 1.8

Table 4. Influence of the methanol: oil molar ratio on biodiesel yield

Runs	Methanol: oil molar ratio	Biodiesel yield (%)
1	3:1	62.1 ± 1.1
2	6:1	95.3 ± 1.2
3	9:1	94.2 ± 1.3
4	12:1	93.1 ± 0.9

Table 5: The physical and chemical properties of the prepared biodiesel

Property	Unit	ASTM D6751	EN 14214	Prepared biodiesel
Relative density at 15 °C	kg/m ³	860-894	860-900	886
Kinematic viscosity at 40 °C	mm ² /s	1.9-6.0	3.50-5.00	3.69
Flash point	°C	> 120	> 120	152
Moisture content	wt. %	<0.05	<0.05	0.008
Cetane number		>47	>51	53
Acid number	mg KOH/g	≤0.5	<0.5	0.25
Glycerol	wt. %	0.02	0.02	<0.015

Figures.

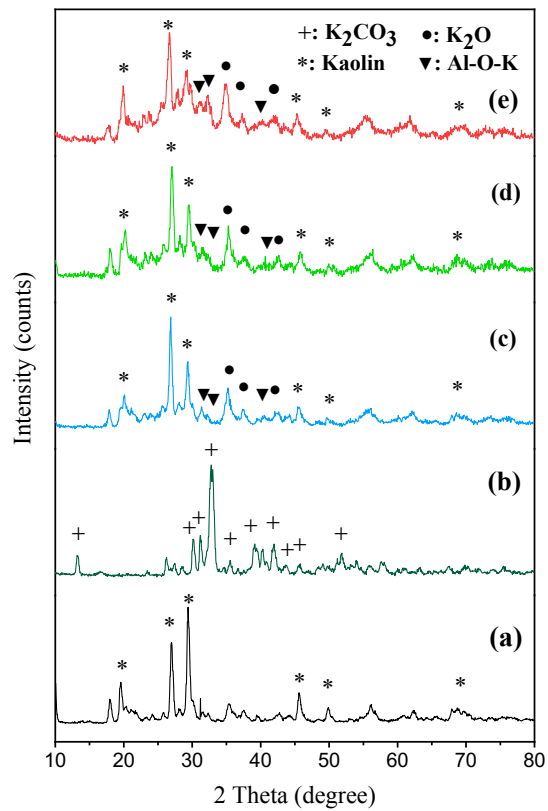


Fig 1. XRD patterns of the kaolin (a), K₂CO₃ (b), K₂CO₃(10%)/kaolin (c), K₂CO₃(20%)/kaolin (d), K₂CO₃(30%)/kaolin (e).

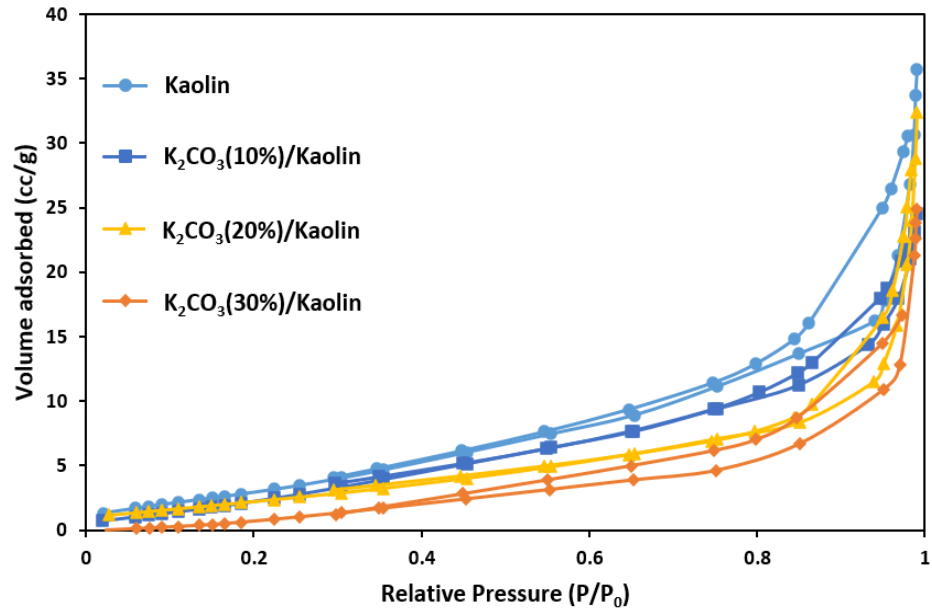


Fig 2. Adsorption/Desorption isotherms of K_2CO_3 /kaolin with various K_2CO_3 loading levels

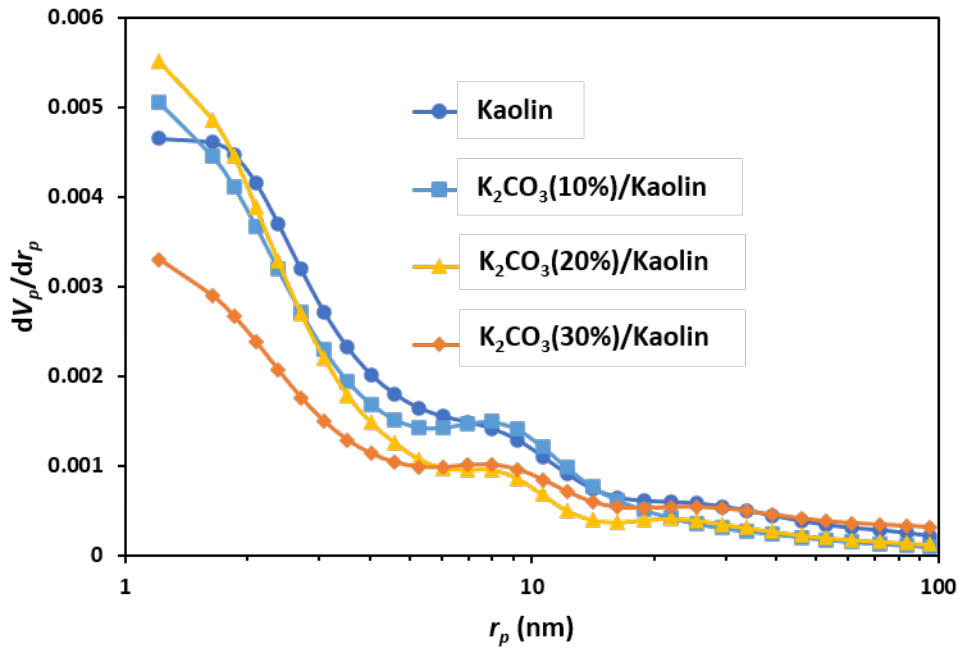


Fig 3. BJH plots of the kaolin and K_2CO_3 /kaolin with various K_2CO_3 loading levels

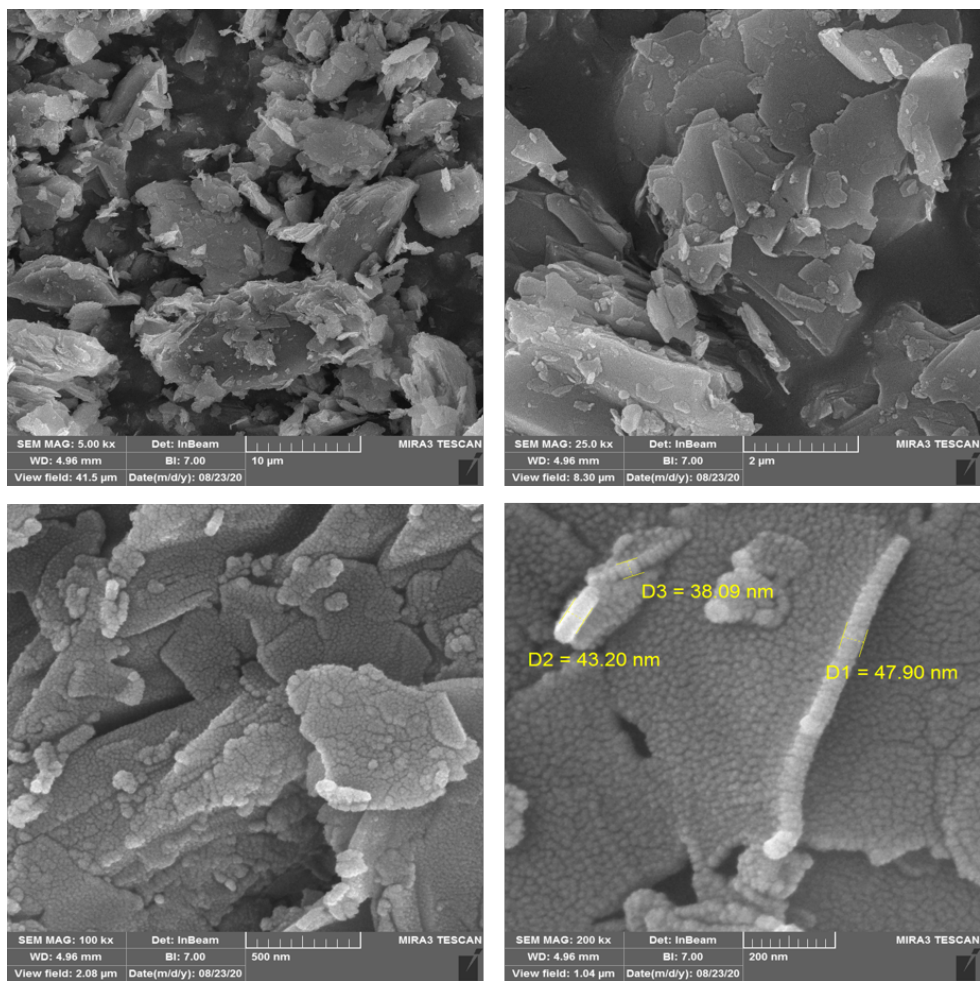


Fig 4. SEM images of $K_2CO_3(20\%)/kaolin$ catalyst.

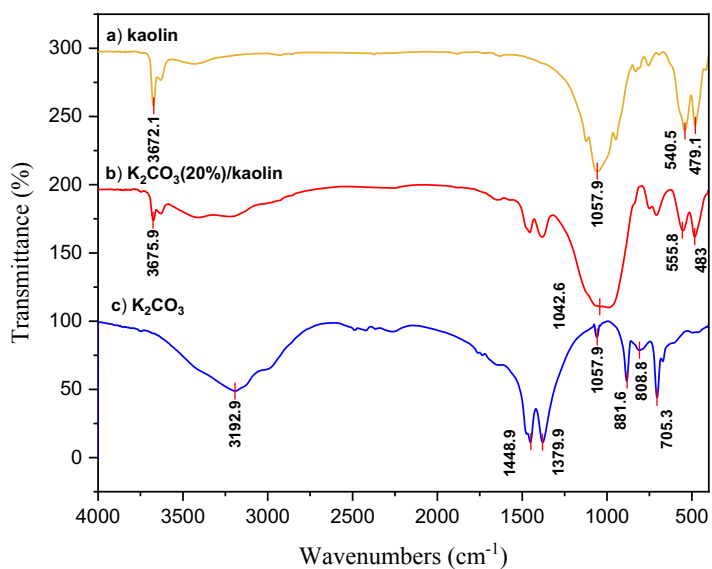


Fig 5. FTIR spectra of kaolin, K_2CO_3 and $K_2CO_3(20\%)/kaolin$ catalyst

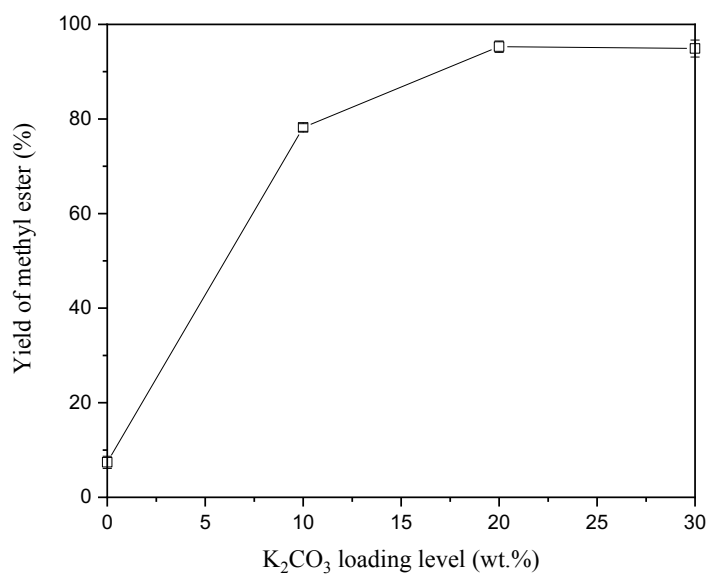


Fig 6. Effect of K_2CO_3 impregnation level on methyl ester yield. The standard %error range is $\pm 0.8-1.8\%$.

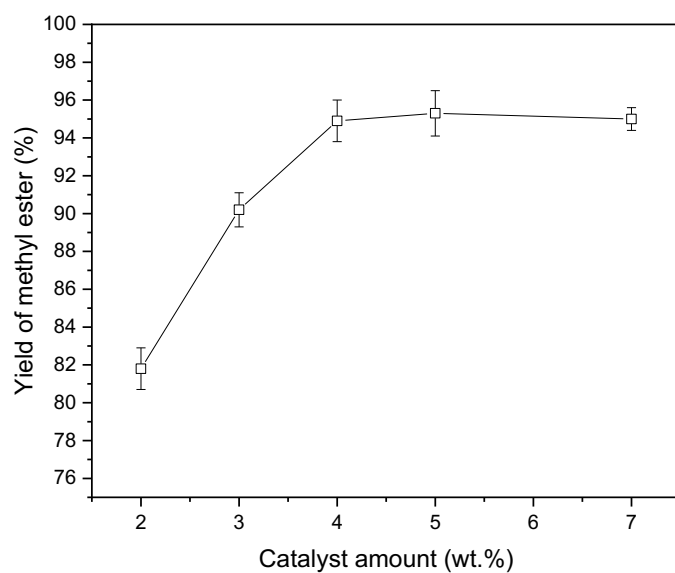


Fig 7. Influence of catalyst amount on yield of methyl ester. The standard %error range is $\pm 0.6-1.2\%$.

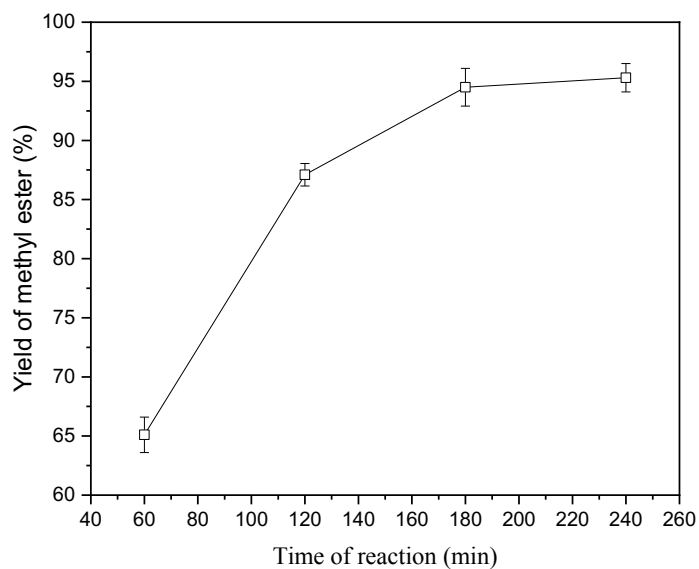


Fig 8. Effect of the reaction duration time on yield of methyl ester. The standard %error range is $\pm 0.9-1.6\%$.

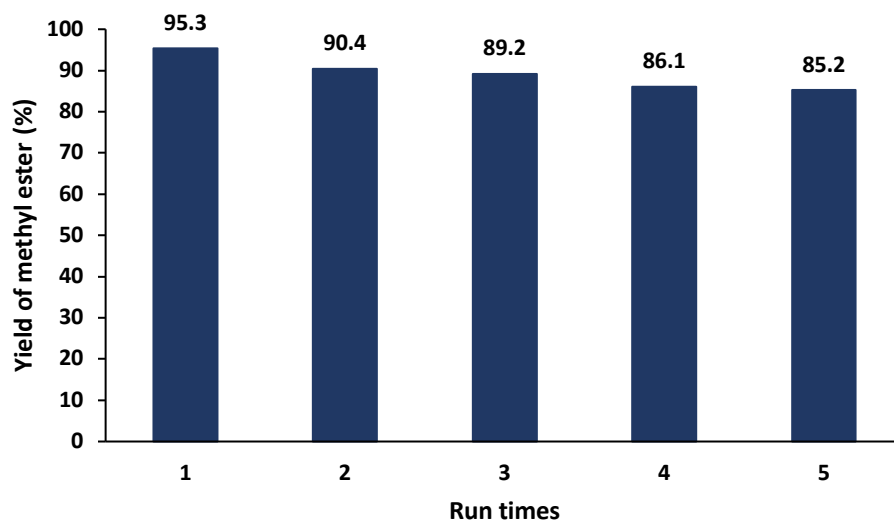


Fig 9. Reusability of $K_2CO_3(20\%)$ /kaolin catalyst. The standard %error range is ± 0.5 -
1.4%.