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Catalyzation of Esterification Reaction Using Sulfated Titanium Dioxide Nanotubes, Experimental Design and Performance.

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ABSTRACT

Titanium oxide nanotubes (TNTs) were prepared by the thermal method and treated with sulfuric acid using microwave proceed to obtain sulfated titanium oxides nanotubes (STiO$_x$NTs). The prepared nanomaterials were characterized using XRD, TEM and IR spectroscopy. Esterification reaction of octanol and acetic acid was applied using sulfated titanium oxides nanotubes (STiO$_x$NTs)as a catalyst, various parameters were studied to obtain the optimum conditions of the esterification reaction using this new kind of nanocatalyst. The synthesis of Octyl acetate by esterification reaction was developed by **F**actorial **D**esign and **R**esponse **S**urface **M**ethodology (FDRSM). Selection of factors was based on the operating conditions that have a significant influence on esterification process, such as temperature; molar ratio and nanotube catalyst. The results indicated that the highest conversion reached to 99.6 % using molar ratio 5:1 octanol to acetic acid at room temperature 22 °C and catalyst 0.7 wt.%, which is matched with the experimental design by factorial design software.

Keywords: Titanium oxide nanotubes, Sulfated titanium oxides nanotubes, Esterification.

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INTRODUCTION

Acid catalysis covers a wide range of industrially important reactions. Homogeneous catalysts such as sulfuric acid, and heterogeneous catalysts such as ion-exchange resins (IERs), are generally employed in conventional esterification processes [1]. Homogeneous acid catalysis is effective; however, it suffers from severe drawbacks such as equipment corrosion, neutralization of the reaction mass, and separation of catalyst from the product stream. In general, these complications have been overcome through the use of heterogeneous catalysts such as strong acid ion-exchange resins [2,3]. IERs are non-corrosive and easy to separate from the reaction mixture. The catalysis by cation-exchange resins offers several advantages over homogeneous acid catalysts. They are easily removed from the reaction medium and can be recycled. In addition, the matrix effects allow reaction selectivity and reduce or eliminate undesirable side reactions. They also offer the possibility of developing non-corrosive processes due to their eco-friendly nature. These catalysts can also be used repeatedly over a prolonged period without any difficulty in handling and storage them [3]. These catalysts are usually styrene-based sulfonic acid or persulfonic acid-based polymeric catalysts. Recently, organosulfonic acid-functionalized mesoporous silicas have shown potential for use as a catalyst for methyl ester formation [1-3]. A variety of materials have been used as solid acid catalysts such as clays, zeolites, sulfated metal oxides, heteropoly acids, etc. The structure of heteropoly compounds has received much attention as solid acid catalysts for both homogeneous and heterogeneous reactions due to their high acid strength and high thermal stability [1-3].

Nowadays nanomaterials gain important interest in many areas of applications; cancer therapy [4], water treatment and desalination [5-9], water splitting for hydrogen production [10-13], bioactivity [14], biosensor [15]. One-dimensional nanostructured "Nanowires, nanorods, nanotubes." are consider one of the most interested nanostructures and gain extra interest for various applications [16,17]. TiO_2 nanotubes consider one of the most important catalysts in many areas of applications compared with colloidal or other forms of titania [6-9]. The tubular structure, large surface-to-volume ratio, and high sedimentation rate are distinct properties of TiO_2-NTs [6-9]. As a result, TiO_2-NTs are more suitable as a catalyst or catalyst support for heterogeneous catalytic reactions and other applications [18]. Moreover, the TiO_2 catalyst is readily available, non-toxic, and shows a relatively high chemical stability and low cost [19].

Modification process was used to improve the catalytic activity of TiO_2; TiO_2–Al_2O_3 catalysts prepared by a co-precipitation method were used for the formation of n-butyl lactate with a good yield by the reaction between lactic acid and n-butanol [16]. ZrO_2-modified TiO_2 nanorod composites prepared by hydrothermal method and then further functionalized by sulfate groups. The sulfated nano composite was used as the solid catalyst for esterification of organic acid [17,18]. The prepared nano composite achieved 81.2 % conversion of levulinic acid converted to ethyl levulinate at 110 °C in 2 hrs over a 20 wt.% of ZrO_2–TiO_2 nanorod composite. These results attributed to the presence of sulfate groups on Zr and Ti adsorption site [20-22].

The previous studies of sulfated TiO2NTs were concerned with catalytic activity for water treatment applications. Sulfate functionalized Fe2O3 Nanoparticles on TiO2 Nanotubes were prepared by hydrothermal method and used as photo-Fenton catalyst for water treatment applications. The presence of sulfate groups increases visible light response and surface acidity which enhance the photocatalytic activity of sulfate functionalized nanocomposite [23]. Also, iron oxide decorated sulfated TiO2NTs for catalytic removal of NO with propane at different temperatures (300–500)°C [24].

The studies which were concerned with sulfated TiO_2NTs as a solid catalyst to enhance the rate of esterification process have some limitations according to size-dependent properties of TiO_2 in tubular form and huge surface area.

The aim of this work is to produce new kind of nanocatalyst sulfated titanium oxides nanotubes ($STiO_x$NTs), where this catalyst has cylindrical geometry shape, which can intimate excellent contact between reactants and catalyst and lead to improve the reaction conversion. The experiments were designed using factorial design software, which is an important tool to save time and reduce costs by saving chemicals.

EXPERIMENTAL WORK

Materials

Commercial rutile phase of TiO_2 nanopowder, NaOH, HCl, H_2SO_4 were used in the preparation of sulfated TiO_2 nanotubes to be used as nanocatalyst in the esterification reaction. TiO_2 nanopowder was purchased from Merck and NaOH pellets were purchased from oxford. The used reactants for esterification experiments were Octanol and glacial acetic acid. All chemicals used in the experiments were of reagent grade.

Synthesis of sulfated titanium oxides nanotubes

The titanium oxide nanotubes were prepared by thermal treatment approach where commercial rutile phase of TiO_2 nanopowder was dispersed at 10 M NaOH. The obtained white suspension was transferred to Teflon lined autoclave then thermally treated at 150 °C for 144 h. A white precipitate of TiO_xNTs was obtained and normalized using 1 N HCl then washed by distilled water. The preparation method was described in details elsewhere [19]. For the preparation of sulfated nanotubes; the wished NTs were treated with 0.01 N H_2SO_4 then immersed in concentrated sulfuric acid with molar ratio 3 ml concentrated H_2SO_4 : 1 gm NTs. The mixture was turned to 1200 W microwave device for 15 min. then fired at 300 °C for 3 hrs to obtain $STiO_xNTs$.

X-ray diffraction (XRD)

The raw TiO_2 powder and prepared TiO_x nanotubes (TiO_xNTs) were analyzed by the X-ray diffraction analysis which is Brukurd 8 advance, and CuK, target with secondary mono chromator λu = 40, mA = 40, and made from Germany. The analysis was carried out for the investigated samples at room temperature. The crystal size was calculated using the XRD peaks with the application of a software computer programmed TOPAZ2 depending on Scherer's formula:

$$L = \frac{0.9\lambda}{\beta \cos\theta}$$

Where **L** is the crystallite size, λ is the X-ray wavelength, β is the corrected FWHM of the diffraction and ϑ is the diffraction angle.

Transmission electron microscopy (TEM)

The prepared sulfated TiO_x nanotubes ($STiO_xNTs$) were characterized by transmission electron microscopy (TEM) analysis (JEOL TEM 2100 high-resolution transmission electron microscope made by Tokyo, Japan) to determine the shape of the ($STiO_xNTs$).

Fourier transforms infrared (FTIR) spectrophotometer

The FTIR analysis of 16 scans per minute at a resolution of 4 cm^{-1} was performed on prepared sulfated TiO_x nanotubes ($STiO_xNTs$). Polytetrafluoroethylene infrared (IR) cards were used to apply transparent films on the sample. The IR data were collected.

Esterification experiments design using factorial design and response surface methodology

The synthesis of Octyl acetate by esterification using sulfated titanium dioxide as a nano catalyst that was developed and optimized following the **F**actorial **D**esign and **R**esponse **S**urface **M**ethodology. The experimental design was a full 2^3 factorial design (three factors each at two levels). Application of this method needs the adequate selection of responses, factors, and levels. The selected response was the acetic acid conversion percentage. Selection of the levels was carried out; where the upper temperature and lower temperatures were 70 and 22 ºC respectively. Molar ratio; octanol to acetic acid levels were 7:1 higher level and 2:1 lower level. Also, the nanotube catalyst was studied where the higher level was 0.7 wt.% and the lower level was 0.2 wt.%.

Accordingly, bath experiments were carried out in a 1,000 ml three-neck flask. One opening is connected to a reflux condenser; another is for feeding and drawing samples while the last is connected with a long leg thermometer to monitor the temperature along the reaction duration. The experiments take place under different parameters such as molar ratio of octanol to acetic acid (2:1, 5:1, and 7:1), temperature (22, 50, and 70) ºC, and weight of catalyst (0.2, 0.5, and 0.7) wt.%. The samples were drawn every 30 minutes, and the produced ester was determined by gas chromatography analysis. The samples of produced ester were analyzed using GC/MS to indicate the product purity. 0.5 ml of diethyl ether and the resulting sample solution is filled in GC autosampler vial and injected in GC/MS to analyze and determine ester percentage in the sample [25].

RESULTS AND DISCUSSION

Characterization of raw and prepared materials

X-ray diffraction (XRD)

TiOxNTs were successfully prepared by hydrothermal method at 150 ºC for 144 h followed by ion exchange process. The raw material (TiO_2 powder) and the prepared nanotubes (TiO_xNTs) were characterized using X-ray diffraction (XRD) analysis to identify phase formation and crystal size determination.

Fig. (1a) and (1b) show the XRD pattern of TiO_2 powder and prepared titanium oxides nanotubes respectively. It obtained that the raw material is pure rutile phase of TiO_2 powder with calculated crystal size 93 nm. Fig. (1a) shows strong and sharp peaks which indicate high crystallinity of the raw material also absences of any peaks related to other TiO_2 phases reveals the high purity of rutile TiO_2 phase. On the other hand, XRD patterns of the obtained TiOxNTs represent different oxides of sodium titanium and titanium oxide nanotubes ($Na_2Ti_3O_7$, $Na_2Ti_6O_{16}$, $Na_2Ti_9O_{19}$, Ti_3O_5) as a result of the thermal treatment process. The presence of sodium titanate forms reveals incomplete ionic exchange process between Na^+ and H^+.

On the other hand, Fig. (1b) shows weak diffraction peaks which indicate low crystallinity of the investigated nanotubes. The crystal size of the synthesized nanotubes was calculated using Scherer's equation and found to be (6.7, 5, 4.5, and 9.6) nm. The presence of different phases of the prepared nanotubes together may lead to high synergetic effect and catalytic activity for practical applications.
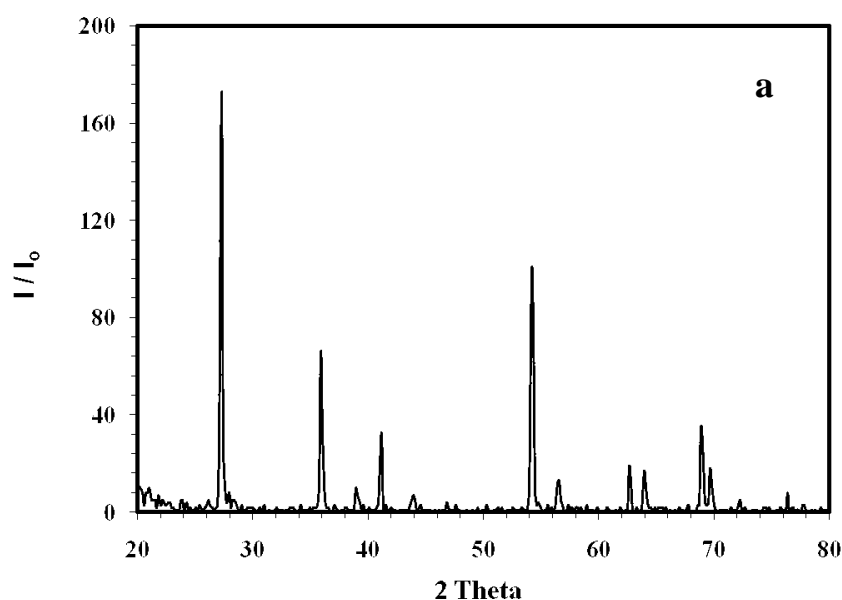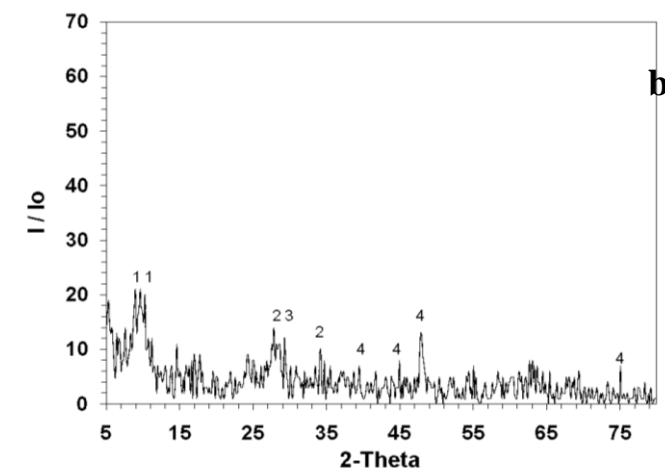
Fig. (1): XRD patterns of:
a) Commercial rutile phase TiO_2 nano-powder
b) Titanium oxides nanotubes, where, (1) $Na_2Ti_3O_7$, (2) $Na_2Ti_6O_{16}$, (3) $Na_2Ti_9O_{19}$, (4) Ti_3O_5

Transmission electron microscopy (TEM)

TEM analysis was used for particles size determination and to study the morphology of the obtained nanotubes. Fig. (2) illustrates TEM of prepared sodium titanium and titanium oxide nanotubes, it can be deduced that the obtained nanotubes have a uniform, hollow and layered structures. The geometry of the obtained nanotubes was measured to be 5 nm inner diameter, 9 nm outer diameter and 141 nm in the length.
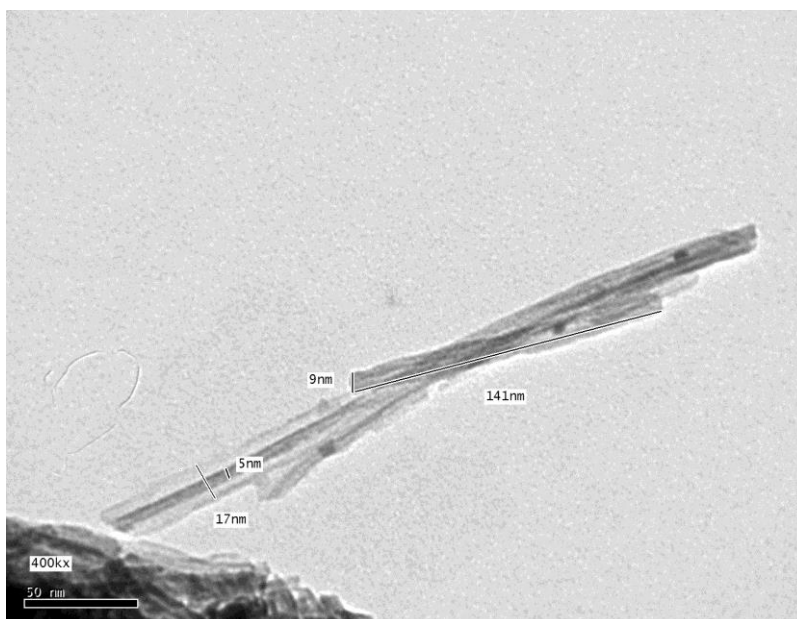
Fig. (2): TEM image of prepared titanium nanotubes

FTIR characterization

IR spectroscopy was used to identify the sulfate S=O species on the surface of TiO_xNTs via the characteristic IR absorption band which are assigned to S=O and O=S=O stretching vibrations. The sulfated TiO_xNTs have Brønsted sites due to the presence of surface protons and Lewis acidity (cationic centers) due to unsaturation in coordination [21,22].

From Fig. (3) it appears that; the sharpness of the peaks indicates that the sulfated TiO$_x$NTs have strong Lewis acid sites. This sharpness attributed to high loading percentage of sulfate [21], which leads to more deficient in electrons due to inviting effect induced by sulfate on the metallic cation [22]. The broadband 3423 cm^{-1} is attributing to the presence of surface OH group. The band found from 1397 to 1305 cm^{-1} is due to the asymmetric vibration of (TiO)$_3$-S=O and (TiO)$_2$-SO$_2$ as a result of stretching vibration of S=O and O=S=O which indicates the presence of sulfate n the surface of TiO$_x$NTs. The shift of characteristic bands (1397 and 1305) cm^{-1} may be attributed to nanotubular structure of TiO$_x$NTs and the preparation conditions [21, 22].
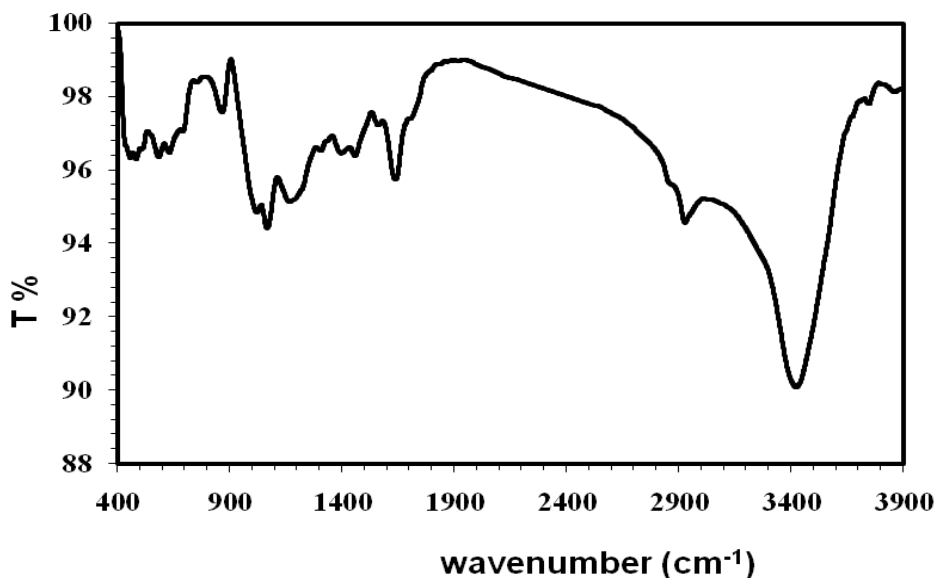
Fig. (3): FTIR spectra of sulfated TiO$_x$NTs

Esterification experiments design using factorial design and response surface methodology

According to **F**actorial **D**esign and **R**esponse **S**urface **M**ethodology (FDRSM) results the experiments run numbers were determined and the operating conditions of each run; revealed that the optimum designed experiments which were 11 runs at the operating conditions as depicted in Table (1).

Table (1): Run sheet according to Factorial Design and Response Surface Methodology for esterification reactions using sulfated nanotube titanium dioxide as a catalyst

Run	Parameters		
	Molar ratio Octanol: acetic acid	Temperature °C	Catalyst: Sulfated TiO$_2$NTs
1	2:1	70	0.2
2	5:1	22	0.5
3	5:1	70	0.7
4	2:1	22	0.5
5	2:1	50	0.7
6	5:1	50	0.7
7	7:1	50	0.2
8	7:1	22	0.2
9	7:1	70	0.5
10	4.5:1	50	0.7
11	4.5:1	22	0.5

According to run sheet Table (1); the experiments of esterification reaction with octanol and acetic acid using nanotube catalyst were conducted to reach the optimum conditions.
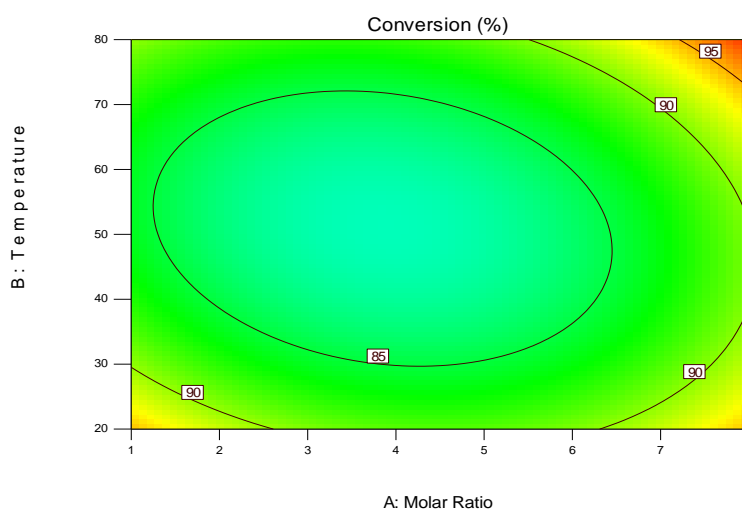
The probability solutions of esterification reaction using **Sulfated TiO$_2$NTs** was studied by **F**actorial **D**esign and **R**esponse **S**urface **M**ethodology (FDRSM).

Fig. (4a) and (4b) indicate respectively counter and the three-dimensional response surface graph of the acetic acid conversion predicted for the experimental range as a function of the temperature of the reaction mixture and the molar ratio of nanotube catalyst 0.5 wt.%. FDRSM solution of this response predicts reaction conversion in the range of 90 to 98 %, where increasing in temperature and the molar ratio can provide increasing in reaction conversion.

Fig. (5a) and (5b) illustrate predicted conversion for another run experiment by the counter and three-dimensional response surface graphs respectively as a function of nanotube catalyst and the molar ratio at fixed temperature 22 ºC. The response of FDRSM solution predicts reaction conversion in the range from 90 % to 95 %, where increasing in the molar ratio of octanol to acetic acid and percentage of nanotube catalyst can lead to increasing in reaction conversion.

Fig. (6a) and (6b) illustrate predicted conversion using FDRSM dimensional counter and response surface graph for the experimental range as a function of nanotube catalyst and temperature fixed molar ratio 7:1. The response of FDRSM solution predicts reaction conversion in the range from 85 % to 99 %, where increasing in temperature and nanotube catalyst weight percentage can increase the rate of reaction, where the conversion increases at short reaction time.

(a)

(b)

Fig. (4): Counter (a) and three dimension response surface plot (b) of conversion as function of temperature and molar ratio of nanotube catalyst 0.5 wt.%

(a)

(b)

Fig. (5): Counter (a) and three dimension response surface plot (b) of conversion as function nanotube catalyst and molar ratio at reaction temperature 22 ºC
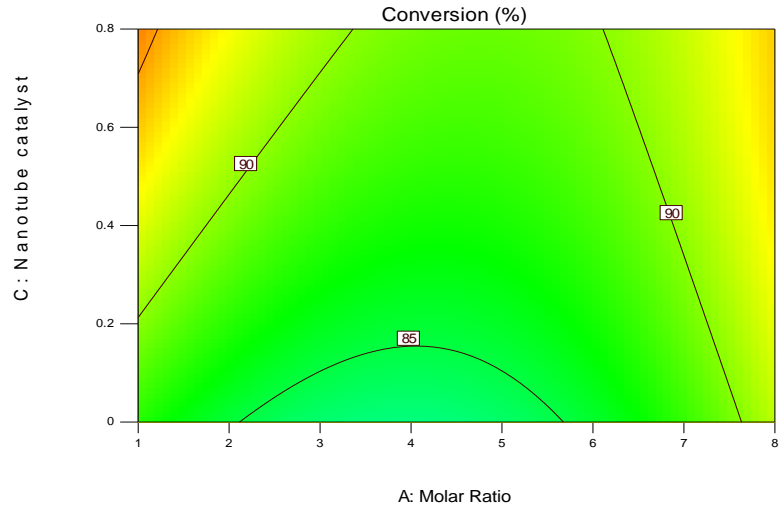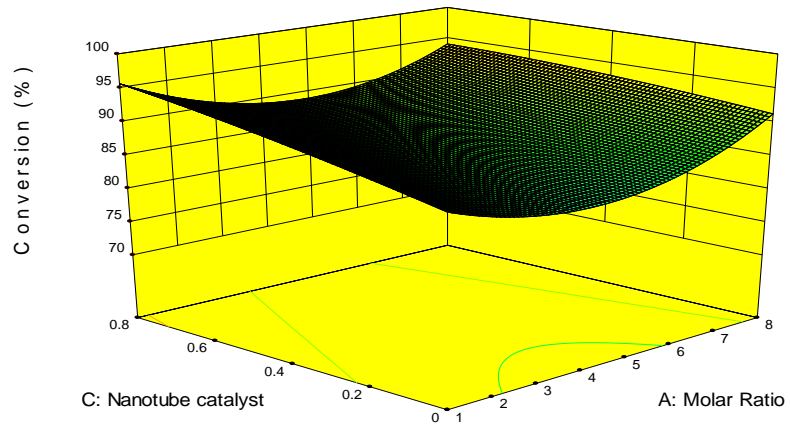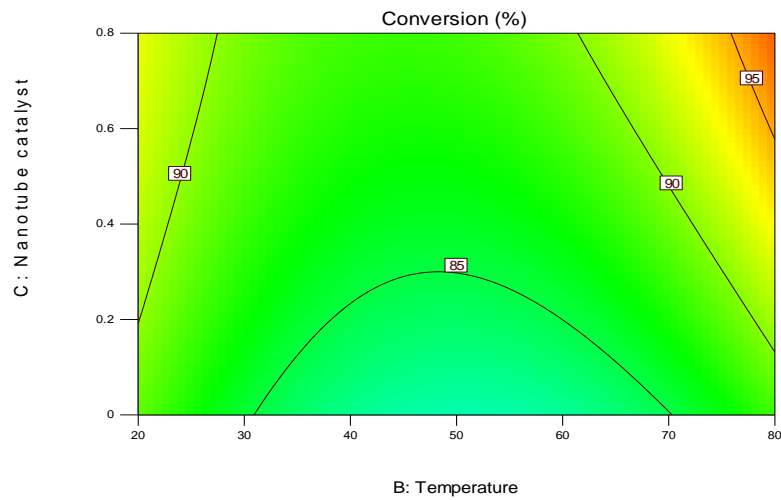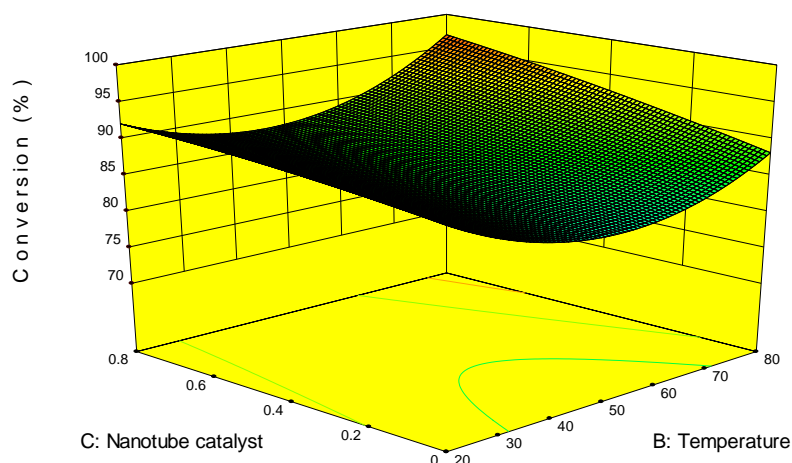

(a)

Design-Expert® Software
Factor Coding: Actual
Original Scale
CONVERSION (%)

99
74.09

X1 = B: TEMP
X2 = C: CATALYST

Actual Factor
A: MR = 7

(b)

Fig. (6): Counter (a) and three dimension response surface plot (b) of conversion as function nanotube catalyst and reaction temperature at molar ratio octanol to acetic acid 7:1

Esterification reaction

Effect of reactant molar ratio

The Batch esterification reaction was conducted at a temperature of 22 °C, 0.5 % nanocatalyst (STiO$_x$NTs) and at a different molar ratio (Alcohol/Acid) 2:1, 5:1, and 7:1. Fig. (7) illustrates the effect of molar ratio on the conversion percent. The maximum ratio was approximately 99 % at MR 5:1 after 15 min, where the reaction conversion is close to MR 5:1 at using MR 7:1 after 15 min but the conversion decreases with time. In this case, increasing in reactant molar ratio can decrease the time of reaction and leads to increase in the reaction rate, which increase the products productivity, according to that the nanocatalyst (STiO$_x$NTs) will absorb more produced water from the reaction mixture, which can lead to deactivation of the nanocatalyst and decrease in reaction conversion [1-3]. The results are matched with the predicted results from FDRSM.
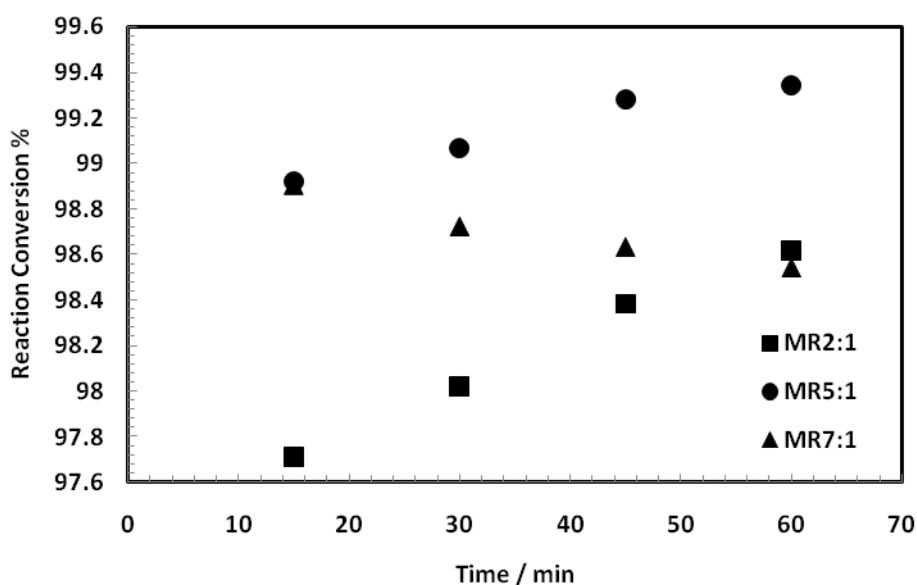

Fig. (7): The effect of molar ratio on the esterification reaction conversion, at temperature 22 °C and nanocatalyst 0.5 wt.%

Effect of temperature

The effect of temperature on conversion was studied at different temperatures namely are: (22, 50, and 70) ºC under fixed molar ratio of octanol to acetic acid (5:1) and fixed nano catalyst 0.5 wt.%. Reaction conversion reached to 99 % after 15 min at temperature 22 ºC, while increasing in temperature leads to decrease in the conversion due to increasing in the catalyst deactivation as shown in Fig. (8). The results are agreement with the predicted results from FDRSM.
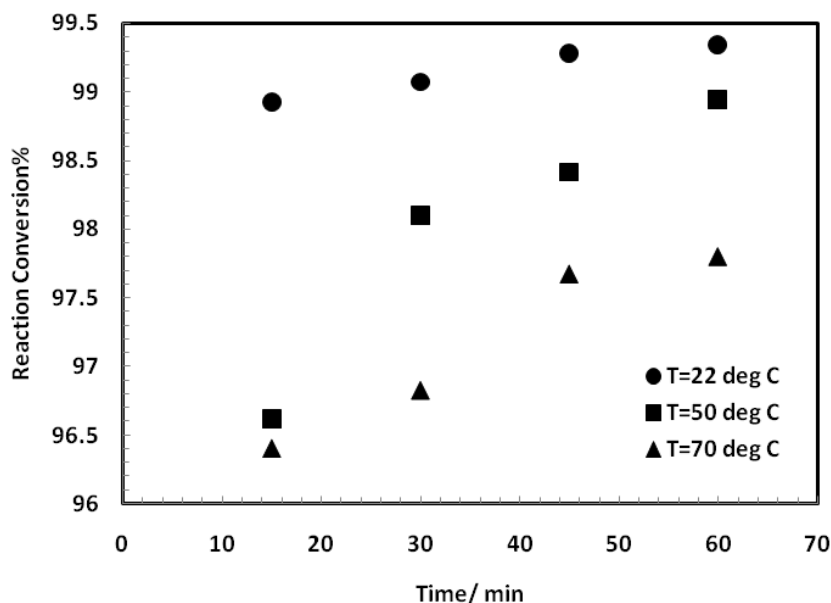

Fig. (8): The effect of reaction temperature on the esterification reaction conversion, at MR 5:1 and nanocatalyst 0.5 wt.%

Effect of catalyst weight percent:

The effect of catalyst percentage was studied at different catalyst weight percentages namely are 0.2, 0.5, and 0.7 wt.% at fixed molar ratio of octanol to acetic acid 5:1 and constant temperature 22 ºC. Fig. (9) illustrates that the catalyst percent 0.7 wt.% provides the highest conversion after 15 min which was 99.6 %, which is matched with FDRSM predicted results.
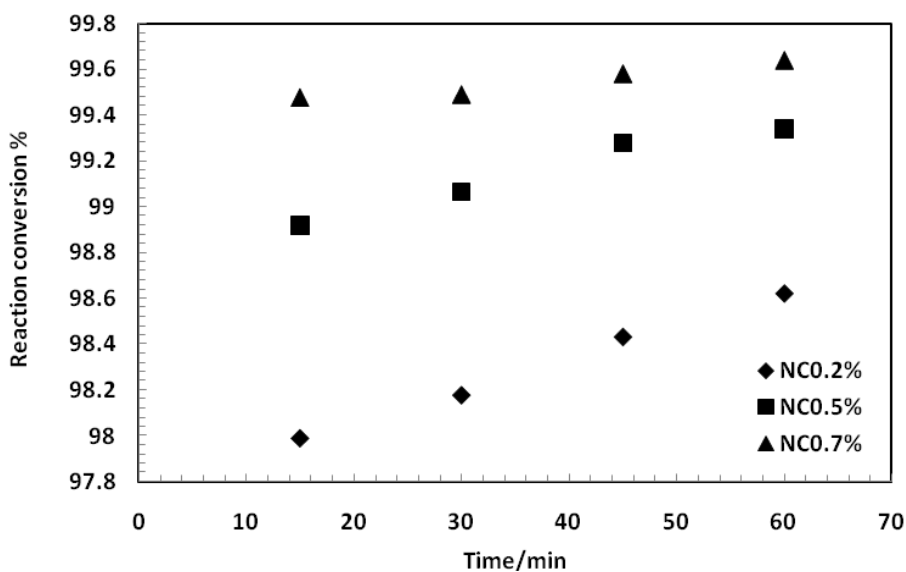

Fig. (9): The effect of catalyst wt% on the esterification reaction conversion, at MR 5:1 and temperature 22 ºC

Estimated low power esterification reactor system using prepared nano-tubes catalyst

The scaling up of the esterification process using new kind catalyst; prepared sulfonated titanium oxides nanotubes (STiO$_x$NTs); was studied according to the best parametric conditions which were molar ratio 5:1 octanol to acetic acid at room temperature 22 ºC and catalyst 0.7 wt.%. Fig. (10) illustrates the estimated new low power esterification reactor system using prepared STiO$_x$NTs. The low power system consists of CSTR reactor ended with hydrophilic nanofiltration membrane to prevent escaping of nano materials from the reactor during operation time and to facilitate filtration of products. After the membrane, the vacuum pump is connected to facilitate separation of the products mixture through the membrane. The bottom of the reactor is connected to pervaporation unit consists of two pervaporation membrane modules to separate the products from unreacted. The low power estimated reactor system is described as follow:

- *CSTR / Nanofiltration reactor:*
  The reactor has two feed opening for alcohol and organic acid; it consists of variable speed mixer for reactants mixing to facilitate the speed changes according to required operation. The esterification reaction is carried out in CSTR/Nanofiltration reactor by two steps. The first step is addition of the reactants in the CSTR reactor and the new nano-catalyst powder (STiO$_x$NTs) is added directly to the reaction mixture, which is suspended in the reaction mixture during mixing, in this case, the reactants intimate excellent contact between them and the nanocatalyst, which lead to high conversion and reduce time of reaction. The reaction can be completed after 1 h, and then the nanocatalyst powder regeneration must be performed. The second step is performed by stopping the mixing in the reactor to facilitate precipitation of nanocatalyst powder on the membrane surface while the vacuum pump works to draw the products and reactants from the reactor to the collecting trap and then to pipe connected to the pervaporation unit to separate the mixture. The membrane is placed in screened holder in the middle of the reactor between the reaction section and the product collecting section, where the membrane module is clamped by flanges to join the three sections (reaction section, membrane section and product collecting section) together. After the reaction and separation of products through the membrane are occurred, the membrane section is separated from the reactor and the membrane with the nanocatalyst powder is dried in a dryer at 110 ºC, then the nan-catalyst powder can be reused.
- *Pervaporation unit*
  Pervaporation unit consists of two pervaporation modules, first one contains the dense selective membrane for produced water and traces organic acid removal [26]. The second module contains another kind of dense selective pervaporation membrane to separate alcohol from ester and the alcohol will be recycled back to the reactor [27]. The separation process is occurred at room temperature, without any heating and the system is under vacuum.

The reaction unit and pervaporation unit are worked at room temperature without the need to heating according to that this system is considered low power and economic system.
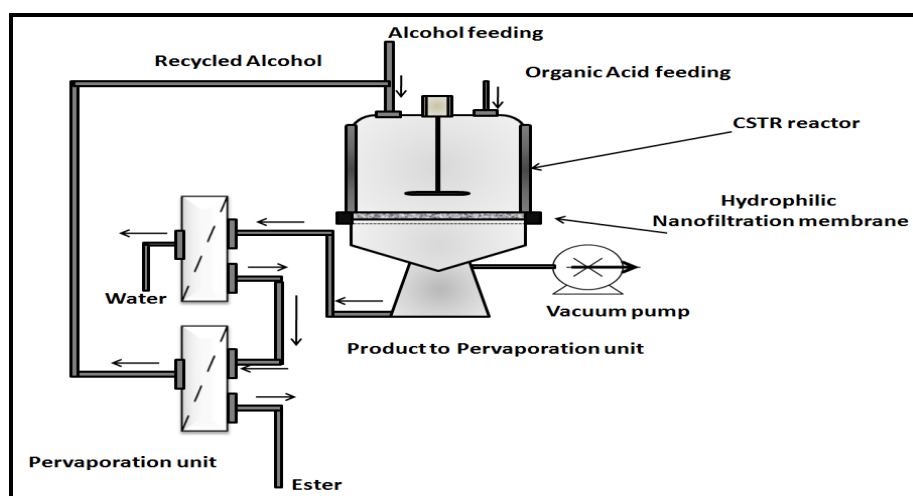

Fig. (10): Estimated esterification reactor system using prepared nano-tube catalyst

CONCLUSION

Titanium oxide nano-tubes (TNTs) were prepared by thermal method then treated with sulfuric acid to obtain sulfonated titanium oxides nano-tubes (STiO$_x$NTs). The sulfated nano-tubes were considered as a nano heterogeneous catalyst for the esterification reaction.

The geometric hollow cylindrical shape provided excellent intimate contact between catalyst and reactants. Esterification reaction of octanol and acetic acid was applied using sulfonated titanium oxides nanotubes (STiO$_x$NTs), various parameters were studied. The optimum conditions were considered molar ratio 5:1 octanol to acetic acid at room temperature 22 ºC and catalyst 0.7 wt.%, where the reaction conversion reached to 99.6 % after 15 min of the reaction time. The experimental results matched with the predicted results from FDRSM.

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