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Thumba methyl ester production using prepared novel TiO_2 nano-catalyst in ultrasonic cavitation reactor

Abhijeet Patil [a,*], Prashant Dhanke[b], Vivek Kore[c], Nitin Kanse[d]

[a,b,c] *Chemical Engineering Department, PVPIT Budhgaon, Sangli (MH) 416 304*
[d] *Chemical Engineering Department, FAMT, Ratnagiri (MH),India 415 639*

Abstract

In this present research, the catalytic activity of the prepared TiO_2 nanoparticles was evaluated towards the thumba methyl ester production by using it under ultrasonic cavitation reactor. TiO_2 nanoparticles were prepared by ultrasonic assisted sol-gel method using titanium tetra-isopropoxide (TTIP) as precursor. The required parameter like ultrasonic irradiation time was varied from 10 to 60 min, power density from 10 W/L- 30 W/L, initial temperature from 5^0C -20^0C and water to TTIP weight ratio from 5-20 for sol-gel method. After completing all the experimental activity, it was found that the morphology of TiO_2 nanoparticles largely depends on the factors such as ultrasonic irradiation time, power density, inlet temperature and water to TTIP ratio. The prepared TiO_2 nanoparticles were useful for the thumba methyl ester production up to 92% conversion of triglycerides from thumba oil in ultrasonic cavitation reactor.

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Keywords: TiO_2 nanoparticles; Thumba Methyl Ester (TME); Ultrasonic cavitation; XRD

1. Introduction

Today's most of the world's energy needs are provided through petrochemical sources, coal and natural gas. All of these sources are finite and at current usage rates, they will become consumed in near future [1].

* Corresponding author. Tel.: +91233-2366398; fax: +91233-2366185
E-mail address: abhijeetpatil.chem@pvpitsangli.edu.in

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Biodiesel (fatty acid alkyl esters) is an alternative fuel similar to diesel. It is obtained from the reaction of vegetable oils or lipids and alcohol with or without presence of a catalyst. Biodiesel is a biodegradable; environment friendly non-toxic, sulphur-free fuel [2-3]. It has similar flow and combustion properties compared to diesel but with low emission behavior. It is very easy to handle safely because it is low in volatile compound content and has high flash point [4]. Fatty acid alkyl esters can be produced by means of various conventional methods like alkali catalyzed, acid catalyzed and lipase catalyzed. Considering these limitations, there is a need to develop an efficient, time-saving, economically functional biodiesel production method. The raw material utilized on commercial basis is edible or non –edible oils obtained from rapeseed, soybean, palm, coconut or linseed. But these sources are non viable in India. While optimizing biodiesel process, Thumba (Citrullus Colocynthis) seed is an unutilized perennial creeper which grows in hot Indian arid zone of Rajasthan and Gujarat

Various types of nano-catalyst have a great demand in the various industrial fields due to its unique properties. The most important nanomaterial is Titanium dioxide (TiO_2) which possesses an optical and dielectric property useful to use it as a photocatalyst in waste water treatment and biofuel production [5]. It is well known that final properties of these nanomaterials depend upon size, crystalline phase and morphology of nanopowder used. TiO_2 nanoparticles occur in three main crystallographic phases, i.e. anatase, rutile, and brookite. Various methods such as sol-gel, solvothermal and hydrothermal method are used in the preparation of TiO_2 nanoparticles

The use of such nanoparticles in biodiesel synthesis helps to promote secondary atomization which results in lower engine emissions, increases evaporation rate and shortens delay period [6-11]. It also provides the catalytic activity during a combustion process. Nano-sized TiO_2 particle has the ability to hold energy within which results in improved reactivity and its large specific surface area improves the combustion characteristics [12-18]. Ultrasonic cavitation is an effective tool to improve the mixing between immiscible oil-alcohol-catalyst.

This work represent the synthesis of TiO_2 nanoparticles by the hydrolysis of TTIP under ultrasonic assisted sol-gel method and how TiO_2 nanoparticles are effective in improving the conversion of triglyceride for thumba methyl ester production. The effect of varying ultrasonic irradiation time, power density, inlet temperature and water to TTIP ratio on the morphology of TiO_2 nanoparticles is also reported. Change in molar ratio as well as catalyst concentration with respect to conversion of triglycerides for thumba methyl ester production is also reported.

2.0 Material and Method

2.1 Materials

99% pure titanium tetra-isopropoxide was purchased from S.D.Fine-Chem. Ltd., Mumbai, India. 99% pure methanol was purchased from nearby local soap industry. Raw Thumba oil was purchased from soap industry of Jodhapur of Rajasthan (India). The oil was filtered to remove the impurities if any through a filter press. The fatty acid composition of raw thumba oil was evaluated using Gas Chromatograph (Make-Netel India Ltd) using EN14103 method. The standard calibration chromatograph used in fatty acid composition analysis is indicated in Fig.1 [13]. It showed that Palmitic Acid account to be 9.56%, Linoleic Acid to be 61.05%, Behenic Acid to be 3.33%, Oleic Acid to be 18.34% and Stearic Acid to be 7.72%. As linoleic acid accounted to be more, it was considered as major component for calculating the conversion of triglycerides. Conversion of triglycerides was considered as amount of linoleic acid reacted per unit amount of linoleic acid in oil charged [13].

2.2 Preparation of TiO_2 nanoparticle by ultrasonic assisted sol-gel method

TiO_2 nanocatalysts particles were prepared in tip type ultrasonicator by sol-gel method. The titanium tetra-isopropoxide (TTIP) was used as a source of TiO_2 and water was used as solvent [13]. A probe type ultrasonicator (Sonics Vibracell VCX-500, USA) with the frequency of 20 kHz was used. In this ultrasonicator, a tip horn was used to produce the ultrasonic irradiation between the reactor and sol-gel mixture. The hydrolysis of titanium isopropoxide took place under ultrasonic irradiation in 1h in a continuous mode.

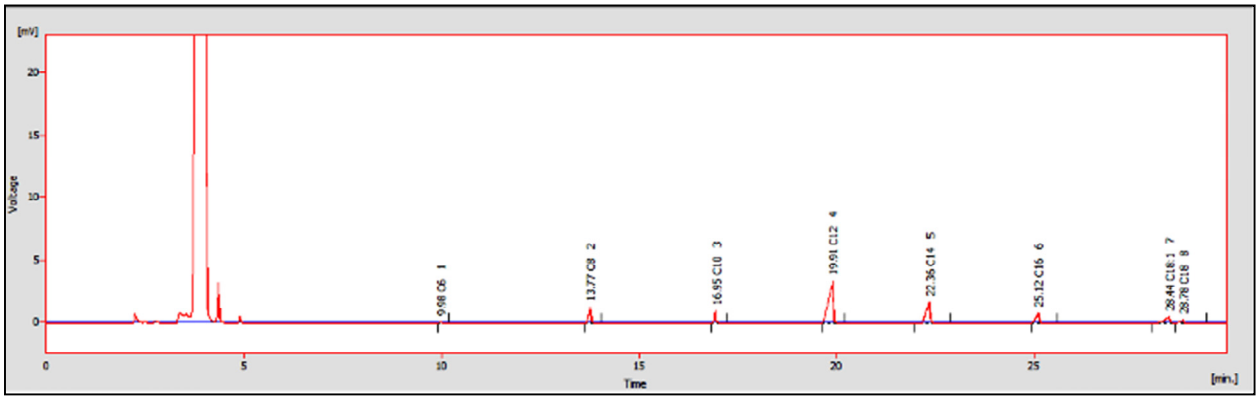

Fig.1 Standard Calibration Chromatograph used in fatty acid Composition Analysis[13].

The initial temperature of the reactor was maintained at around 5^0C -20^0C using a cooling device as per the requirement. The ultrasonic irradiation time was varied from 10 to 60 min, power density from 10 W/L- 30 W/L [13]. The water to TTIP weight ratio was varied from 5-20 as per the requirement of different runs. Slow hydrolysis of TTIP under cold temperature is the most suitable condition for the synthesis of TiO_2 nanoparticles so that the prepared nanocatalysts were kept for slow hydrolysis for 15 h at room temperature followed by drying for 10 h at ambient temperatures. The prepared catalyst was further dried and calcined 600^{o}C in a muffle furnace under the continuous flow of air for 3 hrs.

2.3 TiO_2 Characterization

Pure TiO_2 nanoparticles were completely analyzed by using powder X-ray diffractometer (Phillips PW 1800. 6-80^o). The Cu-Kα radiation (LFF tube 35 kV, 50mA) was selected for the analysis. The crystalline structure and morphology (anatase, rutile and, brookite) of the TiO_2 nanoparticles was reported. A Micromeritics BET analyzer (Micromeritics, ASAP 2020, USA) was used to determine BET surface area, pore-volume, pore-size distribution, porosity and the pore diameter [14].

2.4 Thumba methyl ester synthesis in ultrasonic cavitation reactor [13]

The prepared TiO_2 nanoparticles were used as a catalyst in the synthesis of thumba methyl ester production. Transesterification reaction was carried out in 500 ml three necked flask equipped with reflux condenser and attached to low-frequency horn type ultrasound set up. The experimental set up included a low frequency horn type reactor attached with a transducer that generates ultrasonic jets in the mixture. The horn of transducer was submerged in the flask at a certain level. The flask containing reaction mixture was supported on supporting tray. The time limit is ranging between 20 min to 60 min. The submerged irradiating surface area of the horn was 15 cm^2 with operating intensity of 1.5 W/cm^2. The optimum values of process parameters like methanol to oil ratio, catalyst concentration were reported. The molar ratio of oil to alcohol was varied from 1:4 to 1:10 and the catalyst concentration was varied as 1.0, 1.1, 1.2, 1.3, and 1.4 (Weight % of oil).The temperature of reaction mixture was controlled by means of the water bath. Temperature was maintained inside the flask at 60^0C. The TiO_2 nanoparticles in required quantity was initially added with methanol in required proportion of different experiments [7] and then this mixture was transferred to 500 ml three-necked flask/ reactor already containing raw Thumba oil. The reaction was carried at required temperature for a period of 40 to 60 minutes. After completion of the reaction, it was followed by gravity separation, filtration and distilled water wash. Washing was done for 6 to 10 times. The excess methanol was removed from ester phase by simple distillation due to the large difference in their boiling points.

2.5 Fatty acid composition Analysis of Thumba methyl ester

The water free FAME layer was analyzed by Gas Chromatograph (Make-Netel India Ltd) using EN14103 method to calculate the conversion of triglycerides and yield of biodiesel obtained.

3. Result and Discussion

3.1 Ultrasonic assisted sol-gel method of TiO2 nanoparticle synthesis

More no of experiments were carried out to synthesize TiO_2 nanoparticles by the hydrolysis of TTIP under ultrasonic assisted sol-gel method. The effects of variation in ultrasonic irradiation time, power density, initial temperature and water to TTIP weight ratio on the morphology of TiO_2 is studied.

3.1.1 Effect of ultrasonic irradiation time

Effect of ultrasonic irradiation time for the synthesis of TiO_2 nanoparticles plays important role in morphology of TiO_2. The ultrasonic irradiation time was varied from 10 to 60 min. The water to TTIP ratio was maintained as 10:30. The XRD patterns of the TiO_2 nanoparticle at 40 min irradiation time is shown in Fig.2 which indicates that TiO_2 nano particles under different ultrasonic irradiation times possessed mostly anatase and brookite phases[14]. There was a gradual increase rutile phase with the increase in ultrasonic irradiation time. Fig.3 shows that surface area was decreased after 50 min ultrasonic irradiation time due to large particle size, small pore size and rutile phase morphology. Fig. 4 shows that the crystalline size was also decreased upto 30 min irradiation time and then gradually increased with increase with increase in rutile phase. Highest BET surface area obtained was 111 m^2/gm within 40 min with good crystalline size of 11nm. Increase in irradiation time favours high-velocity interparticle collisions among the particles and prevents the formation of larger particles. This indicates the importance of ultrasonic irradiation in the synthesis of nanoparticles

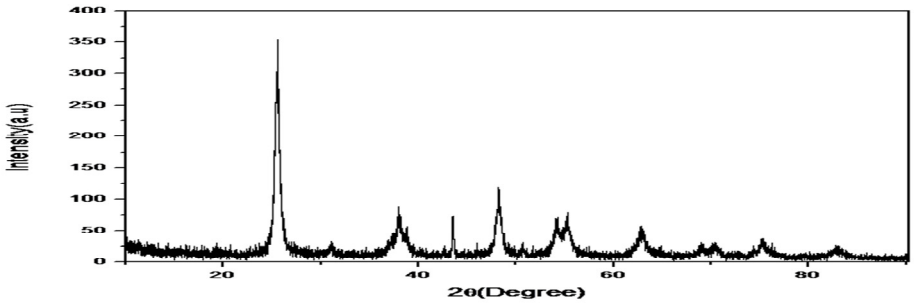

Fig.2 XRD pattern of TiO_2 catalyst prepared by sol-gel method calcined at 600°C for 3h, 40 mins irradiation time

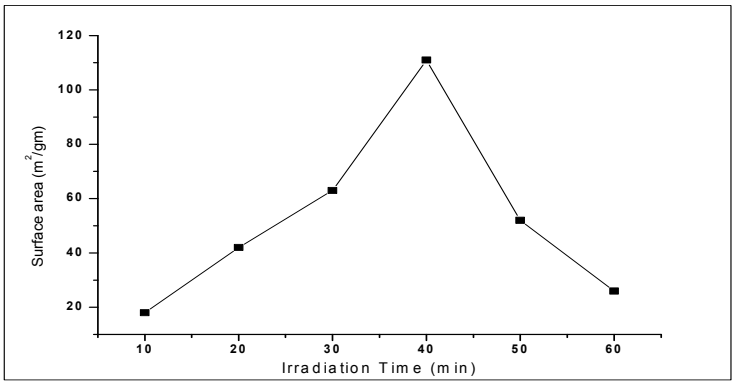

Fig.3: Effect of irradiation time on surface area

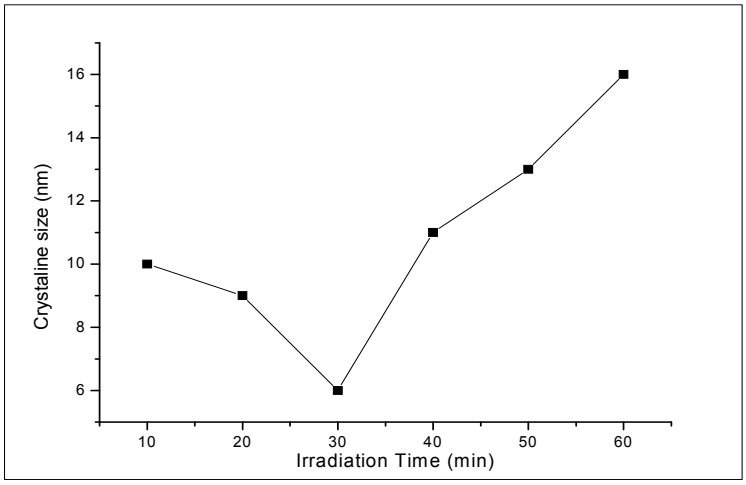

Fig.4: Effect of irradiation time on crystalline size

3.1.2 Effect of power density

The power density was varied from 10 W/L- 30 W/L constant frequency output of 20 kHz. Higher power density means higher energy is supplied to the reactor system. The ultrasonic irradiation time was kept at 40 min. The initial temperature was kept at 15^0C. Table 1 gives details about variation in power density. It shows that the average particle sizes of TiO_2 and pore-size were increased from 6 to 11 nm and 2 to 3.8 nm respectively with an increase in the power densities. The rutile phase was also obtained at a power density of 10 to 30 W/L which indicated that TiO_2 prepared possessed good crystalline size. Surface area was decreased due to the presence of rutile phase along with the other two phases with large a crystalline size of TiO_2 particles [1,13]

Table 1 Characterization of TiO_2 calcined at 600^oC for 3h

Power density (W/L)	**Crystalline size (nm)**	**Pore diameter (nm)**	**Surface area (m^2/gm)**
10	6	2	88
20	9	3.2	64.8
30	11	3.8	49.3

3.1.3 Effect of initial temperature

The initial temperature was varied in the range of 5^0C-20^0C at an interval of 5^0C and power density and irradiation time was kept constant at 30 W/L and 40 min respectively. It is well known that slow hydrolysis at lower ice-cold temperature is best condition for the preparation of well crystalline TiO_2 nanoparticles [12, 13]. The details of morphology are mentioned in Table 2. It was clear that as the initial temperature was increased brookite phase of TiO_2 nanoparticle was increased from 8% to 44% with no rutile phase. This may be because catalyst was calcined for 3h at high temperature of 600^oC. It could be observed that initial temperature also plays a vital role in deciding the morphology of TiO_2 nanoparticles. It was found that 15^oC was an optimum temperature with good crystalline size of 6.7 nm.

Table 2 Characterization of TiO_2 calcined at 600°C for 3h at different initial temperatures

Initial temperature (°C)	Crystalline size (nm)	Anatase: Rutile: brookite (%)	Surface area (m^2/gm)
5	10	92:0.0:08	55
10	9	78:0.0:22	58
15	6.7	66:0.0:34	79
20	4	56:0.0:44	86

3.1.4 Effect of Change in Water to TTIP ratio

The ratio was varied in the range of 5-20 with initial temperature and irradiation time of 20^0C and 40 min respectively. From Table 3 and Fig.5, it was observed that crystanality of TiO_2 nano particles changed with a change in water to TTIP ratio. During the ultrasonic irradiation, the free radicals such as OH, H were produced and these are responsible for the degradation of TTIP [14]. The presence of more water content did not enhance the crystallinity TiO_2 nanoparticles hence the particle size was also lowered with increase in water to TTIP ratio. More anatase phase was obtained with the ratio of 10. The surface area was increased with increase in water to TTIP ratio. Thus, the ratio of water to TTIP was found to be an important factor in determining the crystalline size of TiO_2 nanoparticles. During the ultrasonic irradiation, the free radicals such as OH, H were produced and these are responsible for the degradation of TTIP.

Table 3 Characterization of TiO_2 calcined at 600°C for 3h at different water to TTIP ratio

Water/ TTIP	Crystalline Size (nm)	Anatase:Rutile:Brookite (%)	Surface area (m^2/gm)
5	18	66:22:12	28
10	16	64:0.0:36	32
15	12	58:0.0:42	46
20	8	55:0.0:45	52

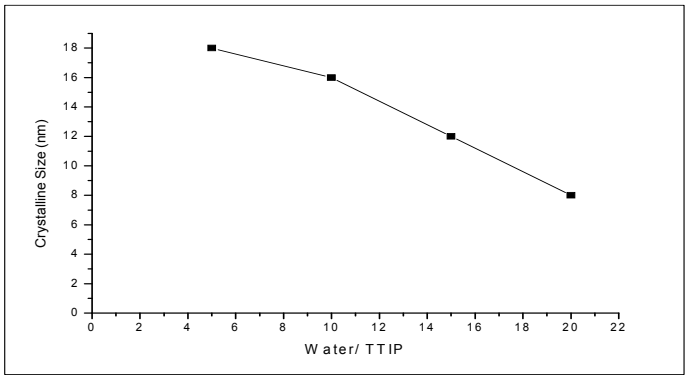

Fig.5: Effect of water to TTIP ratio on crystalline size

3.2 Synthesis of thumba methyl ester using prepared TiO_2 in ultrasonic cavitation reactor

Prepared TiO_2 nanoparticles were used as a catalyst in the synthesis of thumba methyl ester by the transesterification reaction between thumba oil and methanol in ultrasonic cavitation reactor. Experiments were carried out by changing process parameters like alcohol to oil ratio and catalyst concentration and results are reported below.

3.2.1 Effect of change in molar ratio

Three moles of alcohol are required to react with one mole of oil to produce one mole of each ester and glycerol. Molar ratio was varied in the range of 1:4 to 1:10. The reaction temperature was fixed at 60^0C and reaction time was 1h. The catalyst concentration was 1.2% of weight percent of oil. From Table 4, it was clear that conversion increases up to the molar ratio 1:6 and then decreases slightly. It was found that for the molar ratio 1:6 maximum ester yield was 87.5 % in case of ultrasonic cavitation method. The maximum conversion was found to be 92%. Almost 80% conversion of triglycerides was obtained within first 40 mins in case of ultrasonic cavitation method. Molar ratio below 1:6 has not shown good result because of the dominancy of esterification reaction in the initial phases [13]. Higher amount of glycerol was obtained for the molar ratio greater than 1:6 so thumba methyl ester yields and conversion of triglycerides was decreased.

Table 4 Effect of change in molar ratio on conversion of triglycerides

Molar ratio (Oil to alcohol)	**% Conversion**
1:4	85.6
1:6	92
1:8	90.5
1:10	90

3.2.2 Effect of change in TiO_2 concentration

The effect of change in TiO_2 concentration was also investigated in the range of 1.0-1.4% (Weight of catalyst/Weight of oil). The molar ratio was kept constant at 1:6. The temperature was kept constant at 60^0C. From Table 5, it was clear that triglycerides conversion decreases slightly due to increase in TiO_2 concentration. The optimum value of TiO_2 concentration was 1.2% (Weight of catalyst/Weight of oil). The maximum conversion was found to be 92% at 1.2% TiO_2 concentration. Beyond TiO_2 concentration of 1.2%, conversion was decreased due to the formation of some emulsified product. Further increase in TiO_2 concentration increased the viscosity of resulting solution leading to the formation of gels [13]. This hindered the glycerol separation and reduced the conversion of triglycerides and yield of ester.

Table 5 Effect of change in TiO2 concentration on conversion of triglycerides

TiO_2 Concentration (Weight% of oil)	**% Conversion**
1	87.8
1.1	89
1.2	92
1.3	91.5

4. Conclusion

Outcomes of this completed experimental work proved that ultrasonic assisted sol-gel can be used effectively in the synthesis of TiO_2 nanoparticles with more percentage of anatase phases. TiO_2 nanoparticles have more catalytic activity for thumba methyl ester production hence it can be effectively used as a nanocatalyst. Almost 92% conversion of triglycerides was obtained on considering emerged optimum conditions from different experimental work. Ultrasonic cavitation method was found to be an effective, efficient and time saving method where problem of mixing can overcome. The variation in ultrasonic irradiation time, power density, initial temperature and water to TTIP weight ratio significantly affect the morphology of TiO_2. These variations were useful to obtain good crystalline size TiO_2 nanoparticles. Varying operating conditions like oil to alcohol molar ratio and TiO_2 concentration was useful to find out optimum condition for thumba methyl ester production. These optimized operating conditions and higher conversions of triglycerides using these effective techniques make them viable for the industrial sector.

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