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Author(s): Ambat, Indu; Srivastava, Varsha; Haapaniemi, Esa; Sillanpää, Mika

Title: Application of Potassium Ion Impregnated Titanium Dioxide as Nanocatalyst for Transesterification of Linseed Oil

Year: 2018

Version: Accepted version (Final draft)

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Please cite the original version:

Ambat, I., Srivastava, V., Haapaniemi, E., & Sillanpää, M. (2018). Application of Potassium Ion Impregnated Titanium Dioxide as Nanocatalyst for Transesterification of Linseed Oil. Energy and Fuels, 32(11), 11645-11655. https://doi.org/10.1021/acs.energyfuels.8b03310

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Application potassium ion impregnated titanium dioxide as nanocatalyst for transesterification of linseed oil.

Indu Ambat, Varsha Srivastava, Esa Haapaniemi, and Mika Sillanpää

Energy Fuels, Just Accepted Manuscript • DOI: 10.1021/acs.energyfuels.8b03310 • Publication Date (Web): 27 Oct 2018

Downloaded from http://pubs.acs.org on October 29, 2018

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1 2 3		
4 5	1	Application potassium ion impregnated titanium dioxide as nanocatalyst for
6 7 8	2	transesterification of linseed oil
9 10 11	3	
12 13	4	Indu Ambat ^a *, Varsha Srivastava ^a , Esa Haapaniemi ^b , Mika Sillanpää ^a
14 15 16	5	^a Department of Green Chemistry, School of Engineering Science, Lappeenranta University
17 18	6	of Technology, Sammonkatu 12, FI-50130 Mikkeli, Finland
20 21 22	7	^b Department of Organic Chemistry, University of Jyväskylä, Finland
23 24 25	8	*Corresponding Author (email: indu.ambat@outlook.com)
26 27	9	
28 29 30 31	10	Abstract
32 33	11	
34 35	12	The current work comprises the investigation of biodiesel production from linseed oil
36 37 38	13	using TiO ₂ and potassium L-tartrate monobasic ($C_4H_5KO_6$) modified TiO ₂ nanocatalyst. The
39 40	14	different molar ratio of $C_4H_5KO_6$ was selected for TiO_2 modification. The nanocatalyst TiO_2 -
41 42	15	$0.5C_4H_5KO_6$ (1:0.5 molar ratio) showed the best conversion rate for biodiesel. Nanocatalyst
43 44 45	16	was characterized by FTIR, XRD, TEM, BET, XPS and Hammett indicators benzene
46 47	17	carboxylic acid titration method for basicity measurement. The characterization of biodiesel
48 49	18	was performed with GC-MS, ¹ H and ¹³ C NMR. Furthermore, the optimum reaction
50 51 52	19	parameters for transesterification reaction was analyzed and yield was determined by GC-
52 53 54	20	MS and ¹ H NMR. The maximum yield of 98.5 % was obtained at 6 wt% catalyst amount,
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1:6 methanol to oil ratio at 60 °C for 3 hours. The properties of biodiesel obtained from linseed oil were determined using EN 14214/ ASTM D6751 method. The reusability of catalyst was tested up to five cycles and it showed promising results. **Key words**: Biodiesel, linseed oil, transesterification, TiO₂- C₄H₅KO₆ nanocatalyst 1. Introduction The energy crisis is one of the major issue confronted by the whole world due to the dependency on conventional energy reserves^{1,2}. In recent days, with an increase in population results in the expeditious utilization of fossil fuels which leads to two major issues, direct environmental pollution and global warming²⁻⁴. Biodiesel is fatty acid methyl esters (FAME), has been suggested as suitable alternative fuel which is produced by the transesterification of fats/ oils using alcohol mainly methanol or ethanol with a suitable catalyst⁵⁻⁸. FAME can act as a renewable source of energy due to its features such as biodegradability and eco-friendly nature⁹. Generally, vegetable oils, algal oils and animal fat/oils are used as feedstock for biodiesel production¹⁰⁻¹². The feedstock used for the biodiesel production is preferred to be less expensive as well as does not compete with food production^{13,14}. Hence linseed oil was used as feedstock for biodiesel production. Furthermore, the oil content of linseed oil is almost

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similar to edible oil such as rapeseed oil and higher than that of soybean and sunflower oil. Moreover, the content of linolenic acid ($C_{18:3}$) was higher compared to other oils¹³. Kumar et al.,¹⁵ reported 88-96 % conversion efficiency of linseed oil with alkali transesterification. Gargari and Sadrameli¹⁶ observed FAMEs yield up to 98.08% in presence of di-ethyl ether as a co-solvent and calcium oxide as a heterogeneous based catalyst in a fixed bed reactor.

The transesterification reaction is commonly conducted using homogeneous catalyst, heterogeneous catalyst, biocatalyst^{8,9,13,17}. Currently, heterogeneous nanocatalysts attained greater attraction in the field of biodiesel production due to its features such as increased stability, activity, and selectivity^{5,17,18}. Based on previous research reports recommends that potassium doped metal oxides provides promising results in biodiesel production, out of those studies potassium doped on titanium dioxide (TiO₂) using potassium bitartrate as precursor resulted in good biodiesel yield with both edible and non-edible oils^{3,8, 19-22}. Additionally, TiO₂ alone serves as a catalyst for transesterification and also acts as good support in heterogeneous catalysis due to its high chemical stability, thermal constancy and commercial availability^{7,23}. Therefore potassium impregnated on titania using potassium bitartrate as precursor used for biodiesel production from linseed oil.

In the present study is targeted on the production of biodiesel from linseed oil using heterogeneous nanocatalyst. The purpose of our work is to investigate the effect of heterogeneous nanocatalysis on linseed oil, which has not been explored yet. Hence potassium impregnated TiO_2 as a nanocatalyst was synthesized. The loading effect of $C_4H_5KO_6$ on catalytic activity was also investigated. The TiO_2 -0.5 $C_4H_5KO_6$ nanocatalyst showed the significant conversion of linseed oil to biodiesel. The characterization of

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63	synthesized nanocatalyst was done using Fourier transform infrared spectroscopy (FTIR),
64	Scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron
65	spectroscopy (XPS), Transmission electron microscopy (TEM), Atomic-force microscopy
66	(AFM) and Brunauer-Emmett-Teller (BET). Further, the nanocatalyst has been used for
67	transesterification reaction, where the production conditions such as temperature molar ratio
68	of oil and methanol, catalyst amount and time were optimized. The biodiesel was analyzed
69	by gas chromatography with a mass spectrometry (GC-MS), ¹ H and ¹³ C nuclear magnetic
70	resonance (NMR).
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72	2. Materials and methods
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74	2.1 Material
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76	Linseed oil (acid value =0.606 mg KOH/g, average molecular weight=887.9354), titanium
77	oxide nanopowder (TiO ₂), Potassium bitartrate (C ₄ H ₅ KO ₆), methanol were purchased from
78	Sigma-Aldrich. All the chemicals used were of analytical grade
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00	2.2. Symthesis and servening of establist
80	2.2 Synthesis and screening of catalyst
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The titanium dioxide modified by $C_4H_5KO_6$ was synthesized by the impregnation method. In this method, catalysts were prepared by mixing $TiO_2/C_4H_5KO_6$ in different molar ratios of 1:0.25, 1:0.5, 1:0.75 and 1:1. The solutions were stirred continuously for 5h and subsequently dried at 90°C. Finally, dried samples were calcined at 500°C in the muffle furnace (Naberthermb180). The TiO₂, a series of synthesized catalysts by mixing of TiO₂/C₄H₅KO₆ in various molar ratios were screened for fatty acid methyl ester (FAME) production. Furthermore, synthesis of series of the catalyst by doping of various concentration of potassium ion to titania helps to investigate the capability of different catalyst in the transesterification of linseed oil as well as it provides the effect of C₄H₅KO₆ loading on the catalytic activity of titanium oxide.

93 2.3 Characterization of catalyst

The FTIR of catalysts were recorded using Vertex 70 Bruker in the range of 400- 4000 cm⁻¹. TEM images of the samples were obtained using HT7700 (Hitachi). The nanocatalyst was dispersed in ethanol with help of sonication, in order to obtain dispersed particles on the suspension. Later a drop of suspension was added to the carbon-coated copper grid. SEM images of catalysts were recorded by spreading sample on colloidal graphite with 5 kV accelerating voltage (SEM, Hitachi SU3500). XRD patterns were obtained with PANalytical - Empyrean X-ray diffractometer over a 2θ range of $10-120^{\circ}$ with an X-ray source Co-K α of 0.178 nm at 40 mA and 40 kV. The surface area of catalyst was determined using BET (BET,

Micromeritics Tristar II plus). The catalyst samples were degassed at 80°C for overnight to
remove the moisture from the samples.

AFM (Park Systems NX10) images of nanocatalyst were also collected for better illustration of nanocatalyst. The surface composition and the binding energies of elements in nanocatalyst were examined by ESCALAB 250 model XPS with an Al-K X-ray source of 1486.6 eV. The basicity test of catalyst was performed with help of Hammett indicator benzene carboxylic acid titration method. Hammett indicator-benzene carboxylic acid (0.02 mol L^{-1} anhydrous methanol solution) titration method was performed to determine basic strength of synthesized catalyst using Hammett indicators such as neutral red (H 6.8), bromothymol blue (H_7.2), phenolphthalein (H 9.8), 2, 4 - dinitroaniline (H 15)^{24,25}.

114 2.4 Biodiesel production

Linseed oil was used as feedstock for biodiesel production. The screening of different catalyst was done by performing the reaction by mixing oil to methanol in 1:6 molar ratio and with 6 wt % of each catalyst. All the reactions were carried out in a 250ml three neck round bottom flask with mechanical stirrer and reflux condenser at 60°C for 3h. After the reaction, the samples were centrifuged, resulted in three separate phases such as catalyst at the bottom, methyl ester at top and glycerol at the middle. The catalyst was isolated, excess methanol was removed by the evaporator and the obtained biodiesel was analyzed by GC-MS (Agilent-GC6890N, MS 5975) with an Agilent DB-wax FAME analysis GC column

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dimensions 30 m, 0.25 mm, 0.25 μ m. The inlet temperature was 250°C and oven temperature was programmed at 50°C for 1 min and it raises at the rate of 25°C/min to 200°C and 3°C /min to 230°C and then it was held for 23 min. The concentration and presence of ester carbonyl groups of fatty acid methyl esters were determined by ¹H NMR and ¹³C NMR at 400 MHz with CDCl₃ as solvent, respectively. The percentage of linseed oil conversion to fatty acid methyl esters (C %) was determined by the equation given below¹³.

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$$C(\%) = \frac{2 \times Intergration \ value \ of \ protons \ of \ methyl \ ester}{3 \times Intergration \ value \ of \ methyl \ protons} \times 100 \ (Eq. 2)$$

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132 *3.* Result and discussion

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1343.1.Screening and selection of nanocatalyst for transesterification of linseed oil

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136 The selection of nanocatalyst for the biodiesel production from linseed oil was obtained by screening of the catalytic activity of different catalyst such as TiO₂, TiO₂/C₄H₅KO₆ 137 138 (1:0.25, 1:0.5, 1:0.75 and 1:1 molar ratios) at 60°C with 6 wt % of each catalyst and 1:6 oil to methanol molar ratio for 3h. The catalyst composition, surface area, total basicity of 139 synthesized catalyst and catalytic performance of each catalyst was indicated in Table1. Basic 140 141 nature and total basicity of synthesized catalyst was determined by Hammett indicatorbenzene carboxylic acid titration method^{8, 24-26}. The TiO₂ showed no reaction and it is 142 probably due to lower basic strength. Later the basicity of catalyst rises with the loading 143

amount of $C_4H_5KO_6$ that increases the activity of the catalyst. Further increase in the C₄H₅KO₆ amount after optimum value, reduces the catalytic activity possibly due to a decrease in both surface area and basicity. The TiO₂/C₄H₅KO₆ with 1:0.5 ratio showing the significant conversion of biodiesel from linseed oil due to the optimum loading of C₄H₅KO₆. Therefore, TiO₂-0.5C₄H₅KO₆ was selected for the optimization of reaction parameters for higher production of biodiesel.

Table 1.

152 The efficiency of various catalyst for transesterification of linseed oil

No	o. Catalyst	Molar ratio	Total basicity	BET surface	FAME
			(mmol g ⁻¹)	area (m ² g ⁻¹)	conversion (%)
1	TiO ₂	-	0.1	37.58	No reaction
2	TiO ₂ /C ₄ H ₅ KO ₆	1:0.25	0.3	25.43	<5
3	TiO ₂ /C ₄ H ₅ KO ₆	1:0.5	1.80	16.25	98.54
4	TiO ₂ /C ₄ H ₅ KO ₆	1:0.75	1.56	10.65	80.10
5	TiO ₂ /C ₄ H ₅ KO ₆	1:1	0.89	7.37	50.88
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154	3.2. Charact	erization of cataly	st		
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The FTIR peaks of unmodified TiO₂ and TiO₂-0.5C₄H₅KO₆ were shown in Figure 1. In the
 FTIR spectrum of TiO₂-0.5 C₄H₅KO₆ shows new peaks at 895.82 cm⁻¹, 1368.324 cm⁻¹ and
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Figure 2 shows the XRD pattern of both unmodified TiO₂ and TiO₂-0.5C₄H₅KO₆. X-ray diffraction (XRD) analysis of unmodified TiO₂ depicts a good match to standard reference code ICSD: 154607, ICDD: 98-015-4607. XRD pattern of Potassium Titanium Oxide obtained as result of modification of TiO2 with 0.5 molar C4H5KO6 provides a consistent harmony to reference standard code ICSD:73465, ICDD:98-007-3465. The crystallographic parameters of synthesized catalysts are shown in Table 2. Table 2. The crystallographic parameters of unmodified TiO₂ and TiO₂-0.5C₄H₅KO₆.

3	Catalyst	Crystal	a	b	c	α	β	γ
		structure						
			(nm)	(nm)	(nm)			
	TiO ₂	Tetragonal	0.379	0.379	0.941	90	90	90
	TiO_2 -0.5 $C_4H_5KO_6$	Tetragonal	1.02	1.02	0.296	90	90	90



Figure 2. XRD pattern of TiO_2 (unmodified) and TiO_2 -C₄H₅KO₆ (1:0.5molar ratio)

Surface morphology of catalyst was analyzed by SEM. Figure 3a and 3b show the SEM images of TiO₂ (unmodified) and TiO₂-C₄H₅KO₆ (1:0.5molar ratio) with 5kV magnification respectively. By comparing two images, it was observed that there was a significant difference in the structure of TiO₂-C₄H₅KO₆ (1:0.5molar ratio) due to the doping of potassium. The unmodified TiO₂ catalyst looks fluffier and comparatively uniform particles with some aggregates. It is very clear from SEM image of TiO₂- $0.5C_4H_5KO_6$ that flat surface of different shapes was dispersed in the catalytic material indicates a different











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212	The surface area, pore volume and pore size were determined by BET analysis. The
213	surface area analysis of unmodified $-TiO_2$ and $TiO_2 - 0.5 C_4H_5KO_6$ using BET is shown in
214	Table 3. The decrease in porosity of TiO_2 modified with $C_4H_5KO_6$ catalyst was due to the
215	insertion of potassium ions ²⁵ . Even though there is a decrease in porosity and surface area,
216	but there is an increase in catalytic activity for transesterification which is depicted in Table
217	1. It may be due the action of the strength of basic sites in the catalyst ²⁵ . The N_2 adsorption-
218	desorption isotherm for TiO_2 and TiO_2 modified with $C_4H_5KO_6$ from BET analysis is given
219	in Figure 6. The hysteretic loop isotherm indicates the presence of mesoporous materials.

Table 3.

222 The results of Brunauer-Emmett-Teller surface area analysis

	Parameters	Unmodified	TiO_2 - $C_4H_5KO_6$
		TiO ₂	(1:0.5 molar ratio)
Surface area	BET surface area (m ² /g)	37,58	16,25
	BJH adsorption cumulative surface area of	34.32	12.49
	pores (m ² /g)	0.,02	, ->
	BJH desorption cumulative surface area of	34,41	12,75
	pores (m ² /g)		

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227	Figure 6. N_2 adsorption-desorption of (a) unmodified $-TiO_2$ (b) $TiO_2-C_4H_5KO_6$
228	(1:0.5molar ratio)
229	
230	XPS was applied to examine the surface properties and binding energies (BE) of elements
231	in unmodified $-TiO_2$ (b) TiO_2 -C ₄ H ₅ KO ₆ (1:0.5molar ratio). The chemical environment of Ti,
232	O, K were simulated by Gaussian curve-fitting of the Ti 2p, K 2p and O 1s spectra of
233	unmodified $-TiO_2$ and TiO_2 -0.5C ₄ H ₅ KO ₆ . Figure 7 (a) and (b) depicts XPS fitted spectra of
234	unmodified $-TiO_2$ and TiO_2 -0.5C ₄ H ₅ KO ₆ nanocatalyst. Both in unmodified $-TiO_2$ and TiO_2 -
235	$0.5C_4H_5KO_6$ depict Ti 2p signals with two peaks at binding energies of 463.66 and 457.96
236	eV assigned to Ti $2p_{1/2}$ and $2p_{3/2}$, respectively. The BE gap between these two core level
237	orbital suggesting that chemical valance state of Ti in synthesized nanocatalyst is +4. The O
238	1s spectra of unmodified $-TiO_2$ and TiO_2 -0.5C ₄ H ₅ KO ₆ shows binding energy at 530.1 eV,
239	which corresponds to O ²⁺ forming oxide with metals ²⁷ . Figure 7b. represents K 2p with
240	binding energies at 292.37 eV and 294.97 eV which is assigned to $2p_{3/2}$ and $2p_{1/2}$ in the K–O
241	group of TiO_2 -0.5C ₄ H ₅ KO ₆ ²⁸ .
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245	Figure 7 VPS spectre of (a) unmodified. TiO. (b) TiO. C.H.KO. (1:0 5 malar ratio)					
245	Figure 7. Ars	Figure 7. XPS spectra of (a) unmodified $-11O_2$ (b) $11O_2$ -C ₄ H ₅ KO ₆ (1:0.5molar ratio)				
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247	3.3.	Characterization of	f biodiesel			
248	The fatty ac	eid methyl esters r	made from the linseed oil was characterized by GC-MS, ¹ H			
249	NMR and ¹³ C	NMR. The quality	y of the produced biodiesel was tested using the EN 14214/			
250	ASTM D6751	method				
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252	The chemic	cal composition of	of biodiesel was demonstrated with the help of GC-MS			
253	chromatogram	and National Inst	itute of Standards and Technology (NIST) 2014 MS library.			
254	The componer	nt of biodiesel obt	ained after transesterification of linseed oil with $TiO_2 - 0.5$			
255	C ₄ H ₅ KO ₆ was	recognized with the	he help of a library match and represented in Table 4.			
256						
257	Table 4.					
258	The compo	osition of biodiese	l attained after transesterification with TiO_2 - 0.5 $C_4H_5KO_6$.			
Peak	FAM	E	Compound name & mass spectrum			
	Retention time (min)	Library match (%)				
	1	1	19			
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mentioned above. With the help of ¹H NMR, FAME conversion percentage of sample obtained after transesterification with TiO₂- $0.5C_4H_5KO_6$ was found to be 98.5 %. Figure 8a and 8b illustrate the ¹H NMR and ¹³C spectrum of fatty acid methyl esters sample obtained with help of TiO₂- $0.5C_4H_5KO_6$ catalyst respectively. It helps to characterize FAME and can be used to conform the existence of methyl esters in the biodiesel. Moreover, the proposed

catalyst resulted in better conversion of linseed oil to biodiesel in comparison with previously

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reported studies using alkali as well as CaO as solid catalyst ^{15,16}. 269 In ¹H NMR the signal at 3.65 ppm indicates methoxy group (A $_{ME}$) of FAME and signal 270 271 at 2.28 ppm corresponding to methylene group (A_{CH2}). The presence of these signal in the 272 biodiesel sample verifies the presence of methyl ester. Apart from the signal used for the quantification, there are other identifiable peaks such as signal at 0.86 to 0.87 ppm for CH₂-273 CH_3 or for latter methyl group. The peaks in the range of 1.24 to 2.34 represent CH_2 274 (methylene group). The signals at 5.3 range indicate presence of CH=CH (double bond) 275 groups or olefinic groups²⁹⁻³¹. In ¹³C NMR the signal at 174.25 ppm and 51.35 indicates as 276 277 peak for ester carbonyl -COO- and C-O respectively. The unsaturation in biodiesel sample was confirmed with help of signals at 131.88 ppm and 127.05 ppm. In addition to these 278 signals, there are other signals at 14.03 ppm and 14.19ppm indicating the presence of terminal 279 280 -CH₃ groups. The presence of -CH₂ group was showed with help of signals in the region of 22-34ppm²⁹ 281



Figure 8 a. The ¹H NMR for the biodiesel sample obtained with TiO_2 - 0.5C₄H₅KO₆

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4 5	298	
6 7 8 9	299	3.4.1 Catalyst amount (weight %)
10 11 12	300	
12 13 14	301	The influence of catalyst concentration on transesterification was studied by performing
15 16 17	302	reactions at various catalyst concentration from 3 wt% to 12 wt% of the oil. The 98.5 % of
17 18 10	303	biodiesel conversion was obtained within 3 h of reaction time at 60°C by using 6 wt% catalyst
20 21	304	and 1:6 oil to methanol molar ratio (Figure 9a). The conversion of oil to biodiesel depends
22 23	305	on catalyst amount, if the catalyst amount is lower than optimum concentration; there is
24 25 26	306	reduction in FAME conversion due to decrease in the availability of active sites and
26 27 28	307	hindrance to phase separation ^{19,25,32} .
29 30 31	308	
32 33 34	309	3.4.2 Oil to methanol molar ratio
35 36 37	310	
38 39 40	311	Figure 9b depicts that the biodiesel conversion progressively rises from when oil to
41 42	312	methanol molar ratio was increased from 1:3 to 1:6. The reaction was carried out at 6 wt%
43 44	313	catalyst at 60°C for 3h of reaction time. The biodiesel conversion was negatively affected by
45 46	314	increasing methanol concentration above the optimum value which was due to the increased
47 48 49	315	solubility of glycerol to ester phase resulting in difficulty in separation of biodiesel. It may
50 51	316	also favor the reverse reaction than the production of biodiesel ^{33,34} .
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318	3.4.3	Temperature
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320	The effect of temperature on biodiesel yield was investigated by conducting the reaction
321	at various temperatures using 6 wt% catalyst, 1:6 oil to methanol molar ratio for 3h reaction
322	time (Figure 9c). The FAME conversion increased significantly up to 60°C and resulted in
323	an optimum yield of fatty acid methyl esters. After 60°C biodiesel conversion decreased with
324	increase in temperature, which is due to the fact that elevated temperature favors vaporization
325	of methanol ^{25, 35,36} .
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327	3.4.4 Time
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329	The influence of reaction time on transesterification reaction was examined by performing
330	reactions for different time intervals using 6 wt% catalyst, 1:6 oil to methanol molar ratio at
331	60°C depicted in Figure 9d. The percentage of FAME conversion rose with the increase in
332	reaction time up to 180 min and reached at its maximum. After 180 min instead of an increase
333	in the yield of biodiesel, reduction in ester content with an increase in reaction time was
334	observed. This is due to the reversible nature of transesterification reaction. After a prolonged
335	reaction time backward reaction / reverse reaction of transesterification reaction is favored
336	which leads to the hydrolysis of esters ^{35,37} .
337	



3.5. Properties of synthesized biodiesel from linseed oil The properties of linseed oil methyl esters were determined using EN 14214/ ASTM D6751 method as shown in Table 5. All these parameters play an important role in biodiesel quality. The acid value of linseed oil methyl ester was found to be 0.3 mg KOH/g and it was within the limits of EN ISO method. The increase in acid value can create issues like corrosion of rubber parts of engine and filter clogging³⁸. The other two important fuel parameters which influence the fuel injection operation are density and kinematic viscosity. Higher values of this can adversely affect the fuel injection process and result in the formation of engine deposits^{39,40}. The density and kinematic viscosity of linseed oil methyl esters were 891.52 kg/m³ and 3.5709 mm²/s respectively. The other parameter is the flash point which indicates the minimum temperature at which fuel starts to ignite. It is important to know flash point value for fuel handling and storage ⁴¹. The rest of the preferred features such as calorific

value, cloud point, cetane number, and pour point are also within EN ISO/ASTM limits.

Table 5.

Properties of linseed oil methyl esters (TiO₂-0.5 $C_4H_5KO_6$ catalyst at concentration of 6wt%, 1:6 oil to methanol ratio, reaction temperature 60°C, reaction time 3h)

	Property	EN 14214 test	Limits	Methyl ester fron
		method		linseed oil
	Acid value (mg KOH/g)	Pr EN14104	0.5 max	0.3
	Density at 15°C (kg/m ³)	EN ISO 12185	860-900	891.52
	Kinematic viscosity at	EN ISO 3104	3-5	3.5709
	40°C mm ² /s Flash point (°C)	EN ISO 2719	-	173°C
	Cetane Number	EN ISO 5165	≥51	57
	Cloud point (°C)	D2500		4
	Pour point (°C)	ISO 3016		2
	Calorific value (MJ/kg)	D6751		40.89
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63	3.6. Reusability	and stability of cataly	st	
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865	The catalyst reusability	concept makes transe	sterification proc	ess cost effective and
66	friendlier. The catalyst dea	ctivation is mainly du	to deposition o	f impurities, oil conte
67	thermal deactivation. The	regeneration of cata	lyst usually attai	ned with help of su
868	solvent washing and cale	cination ⁴² . To analy	ze the reusabilit	ty of TiO_2 -0.5 C ₄ H
69	nanocatalyst, firstly it was	s separated from line	seed oil methyl	esters and glycerol.

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transesterification, the separated catalyst was washed several times with heptane to remove impurities. The washed catalyst was dried at 90°C and calcined at 500°C for 3h to reactivate the catalyst. The catalytic reusability of TiO_2 -0.5 C₄H₅KO₆ over linseed oil using 6 wt% catalyst, 1:6 oil to methanol molar ratio within 180 min of reaction time at 60°C represented in Figure 10. Linseed oil to FAME conversion was decreased from 98.5% to 93.1%, respectively, in five cycles.

Stability of nanocatalyst after different cycles were evaluated by determining the leached metal ion concentration depicted in Figure 10. Inductively coupled plasma (ICP, Agilent 5110) was used to measure metal concentration. It was detected that from cycle 1 to cycle 5, the Li concentrations in solution are less than 0.043 mg/L. Moreover, Ti concentration in solution was null up to three cycles after that there was a slight leaching of Ti ions to solution which is less than 0.0004 mg/L



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Figure 10. Reusability analysis of TiO₂-0.5 C₄H₅KO₆ catalyst up to five transesterification
 reactions

387 4. Conclusion

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389 The biodiesel was successfully synthesized from linseed oil with help of TiO₂-0.5 $C_4H_5KO_6$. The modification of TiO₂ with $C_4H_5KO_6$ enhanced the properties of nanocatalyst 390 due to impregnation of potassium and showed better conversion in comparison to unmodified 391 TiO₂. FTIR, XRD, SEM, TEM, AFM confirmed the integration of potassium ions to TiO₂ 392 nanostructure. The best activity was obtained at an optimum loading of C₄H₅KO₆ to TiO₂ in 393 0.5:1 molar ratio. The nanocatalyst showed 98.5 % fatty acid methyl ester content using 6wt 394 395 % catalyst amount, 1:6 methanol ratio at 60°C within a reaction time of 3h. The properties of biodiesel such as acid value, density, kinematic viscosity and flash point were within the 396 EN 14214 limits. Thus, FAME obtained was of good quality. All these results supports the 397 398 efficient performance of TiO₂-0.5 C₄H₅KO₆ as a catalyst for the biodiesel production from 399 linseed oil as a feedstock. The reusability of the catalyst also showed a promising result, 400 which makes it economically feasible.

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