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Catalytic synthesis of fatty acid methyl esters from *Madhuca indica* oil in supercritical methanol

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ABSTRACT

Fatty acid methyl esters (FAMEs) that are used as biodiesel can be synthesized in supercritical methylating agents such as supercritical methanol. While the synthesis can be conducted both non-catalytically and catalytically, the synthesis in the presence of oxides is significantly faster. In this study, FAMEs were synthesized by transesterification of a non-edible oil (Mahua, *Madhuca indica*) in supercritical methanol with a wide variety of oxides. The reaction was extensively studied with eleven different oxides, synthesized using the solution combustion method, as catalysts. In addition, the best two catalysts, namely MgO and Mn_3O_4, were synthesized using four different fuels in the combustion synthesis. The catalytic effect of all these oxides was investigated and conversions ranging from 5% to 100% were obtained over the investigated range of temperature from 503 K to 583 K, and with reaction time varying between 2 min and 80 min. Among all the catalysts, MgO synthesized with ascorbic acid as the fuel for the solution combustion gave the best results. Therefore, this catalyst was chosen and the influence of operating temperature for the transesterification reaction (503–583 K) on the rate of the reaction was studied. A pseudo first order kinetic model was obtained based on the proposed Eley-Rideal reaction mechanism and, the rate constants were obtained. The rate constants varied between $1.61 \times 10^{-3}\,s^{-1}$ to $4.93 \times 10^{-3}\,s^{-1}$ with an activation energy of 36 kJ/mol and a pre-exponential factor of $9.33\,s^{-1}$. The rate constant obtained for the non-catalytic supercritical transesterification with oxide as catalyst was significantly higher than the rate constant of $9.9 \times 10^{-5}\,s^{-1}$ obtained for the non-catalytic reaction at 523 K. The activation energy for the catalyzed reaction (36 kJ/mol) was notably lower than the activation energy (75 kJ/mol) for the uncatalyzed reaction indicating the efficacy of the catalyst.

1. Introduction

The energy demands are increasing throughout the world with the industrial and transportation sectors having the highest share in energy consumption [1]. The energy requirements (~80%) of the transportation sector are mainly fulfilled by the fossil fuels. However, it has been predicted that the global fossil oil reserves would deplete within the next 45 years [2]. Further, the greenhouse gas (CO_2) emissions has increased by 92% in the last thirty years [1]. Thus, there is a need to find alternate ecofriendly energy sources that are socially acceptable and also economically viable. Biodiesel, which is a mixture of fatty acid alkyl esters, results in an average reduction of 40% in the emissions when used as the fuel in the diesel engine [3]. Thus, biodiesel is a non-toxic, renewable, biodegradable and low sulfur alternate fuel and has been considered as a cleaner substitute for the diesel [4,5].

The raw materials that are mostly employed for the biodiesel synthesis are edible and non-edible vegetable oils. However, non-edible oils are preferred as these crops can be grown on barn lands, avoiding competition for the land between edible and non-edible crops [6,7]. Transesterification is the preferred method of biodiesel synthesis in comparison to other methods such as dilution, microemulsion and pyrolysis [8]. In transesterification, the triglycerides are converted to fatty acid methyl esters (FAMEs) using a methylating agent through an exchange of the alkoxy moiety either in the presence or absence of a catalyst [9]. Homogeneous catalysts involve either acid or base catalysts but they are sensitive to the impurities present in the feedstock such as water and free fatty acids [2,10]. Further, when the homogeneous catalysts are employed in the reaction the downstream processing for product separation becomes complex, tedious, time consuming and further leads to a large amount of waste water. Moreover, the homogeneous catalysts cannot be reused. Biological catalysts such as immobilized enzymes can also be used but these are expensive and reusability is another issue. However, these limitations associated with the homogeneous and enzymatic catalyst can be overcome by a

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Table 1
Literature available on the transesterification reaction performed under sub or supercritical conditions in the presence of catalysts.

S.N	Oil	SCF	Catalyst	Optimum operating conditions	Yield	Rate constants[a] $(s^{-1}) \times 10^4$	Reference
1.	Sunflower	Methanol	CaO	252 °C, 24 MPa, 6 min, 3 wt%, 41:1	100%	35.2	[80]
2.	Rapeseed	Ethanol	ZnO	270 °C, 15 MPa, 60 min, 42:1, 3 wt%	93%	–	[66]
			CaO	270 °C, 15 MPa, 60 min, 42:1, 3 wt%	88%	–	
3.	Palm	Ethanol	CaO/Al_2O_3	285 °C, 20 MPa, 30:1, 4.85 min	96%	–	[81]
4.	Palm	Methanol	$CaO/KI/\gamma\text{-}Al_2O_3$	290 °C, 12 MPa, 24:1, 3 wt%, 60 min	95%	6.17	[82]
5.	Castor	Ethanol	NaOH	300 °C, 9.52 MPa, 40:1, 10 min, 0.1 wt%	98.9%	164	[83]
6.	Rapeseed	Methanol	SrO, CaO, **ZnO**, TiO_2, ZrO_2	250 °C, 10.5 MPa, 40:1, 1 wt% of ZnO, 10 min	95%	17.3	[48]
7.	Triolein	Subcritical Methanol	Acid exchange resin, Nafion + $SCCO_2$	205 °C, 25 MPa, 25:1, 9 g of catalyst, 2 min	88%	276	[84]
8.	Rapeseed	Methanol	Zinc nitrate (metal precursor for ZnO)	250 °C, 35 MPa, 3 wt% 10 min	96.9%	–	[85]
9.	Palm	Methanol	$SO_4\text{-}ZrO_2$	250 °C, 0.5 wt%, 24:1, 20 min	90%	–	[86]
10.	Soybean	Sub or Supercritical Methanol	Nano-MgO	260 °C, 28 MPa, 10 min, 3 wt%, 36:1	100%	65.2	[87]
11.	Crude rapeseed	Methanol	NaOH	250 °C, 10.2 MPa, 24:1, 6 min, 0.8 wt%	100%	116	[88]
12.	Waste frying oil	Sub or Supercritical Methanol	Zeolite Y solid acid catalyst (molar ratio of SiO_2/Al_2O_3 = 4.88)	240 °C, 12 MPa, 15 min, 5:1, 0.2 g	100%	76.8	[89]
13.	Sunflower	CO_2 + Methanol	CeO_2, WO_3, ZnO, ZrO_2, mixed metal oxides (50–50 wt %), **ZrO_2-SO_4**, $WO_3\text{-}ZrO_2$, $CeO_2\text{-}ZrO_2$, $ZnO\text{-}La_2O_3$, Al_2O_3	200 °C, 20 MPa, 4 min, 25:1, 5 g of $ZrO_2\text{-}SO_4$	98%	163	[90]
14.	Jatropha	Near critical Methanol	Base: Ca & La mixed oxide (CaLaO)	240 °C, 8.2 MPa, 21:1, 10 min, 1 wt% ($CaLa_4$ most active)	93%	27.2	[91]
15.	Palm products (crude palm oil (CPO), refined (RPO), palm fatty acid distillate (PFAD))	Near critical Methanol	$SO_4\text{-}ZrO_2$, **WO_3-ZrO_2**, $TiO_2\text{-}ZrO_2$	250 °C, 24:1 (for CPO and RPO), 18:1 (for PFAD) 10 min, 20% $WO_3\text{-}ZrO_2$ calcined @ 800 °C	91% (CPO), 94% (RPO), 81% (PFAD)	–	[92]
16.	Crude rapeseed	Methanol	Liquid organic amine (ethylene diamine, diethyl amine, **triethylamine**) + co-catalyst (propylene oxide)	250 °C, 8.5 MPa, 24:1, 10 min	89.5%	14.2	[93]
17.	Soybean	Subcritical Methanol	$MnCO_3/ZnO$	(Mn/Zn = 1:1 M ratio) 18:1, 448 K, 1 h, 4 wt% of catalyst	99.25%	9.72	[94]
18.	Soybean	Subcritical Methanol	K_3PO_4	220 °C, 8 MPa, 24:1, 30 min, 1 wt%	95.6%	25.6	[95]
19.	Soybean	Subcritical Methanol	KOH	160 °C, 24:1 0.1 wt%, 10 min	98%	20.9	[96]
20.	Used vegetable oil	Methanol	Cs doped heteropolyacid	260 °C, 20 MPa, 40:1, 40 min, 3 wt% of $Cs_{2.5}PW_{12}O_{40}$	92%	7.26	[97]
21.	Purified palm oil	Near critical Methanol	C based catalyst (synthesized by incomplete carbonization of naphthalene in H_2SO_4)	270 °C, 12:1, 0.5 wt%, 30 min	95%	10.6	[98]
22.	Soybean	Methanol	CH_3ONa	250 °C, 23:1, 1 wt%, 20 min	97.4%	28.8	[68]
23.	Soybean	Subcritical Methanol	Na_2SiO_3	220 °C, 3 MPa, 36:1, 0.5 wt%, 30 min	95.6%	18.3	[52]

[a] Calculated at the optimum operating conditions using the pseudo first order kinetic model (Eq. (16a)).