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Study of 'co-solvent effect' on production of biodiesel from Schleichera Oleosa oil using a mixed metal oxide as a potential catalyst

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ABSTRACT

In this study, biodiesel was prepared from a non edible feedstock using two step process followed by heterogeneous base catalyzed transesterification reaction. A novel solid heterogeneous base catalyst (strontium lanthanum mixed metal oxide) was synthesized via co- precipitation route and was characterized by XRD, FT-IR, SEM, and EDX. The free fatty acid content of the feedstock was assuaged by esterification process followed by transesterification for the synthesis of biodiesel. Effect of co-solvent on biodiesel yield was investigated in each subsequent experiment. Effect of various factors including calcination time, temperature, reaction time, molar ratio (methanol: oil), and catalyst concentration were also taken into account using OVAT (one variable at a time). High quality and pure biodiesel was synthesized at optimized conditions viz. Alcohol to oil molar ratio (14:1), catalyst dose (1.5%), temperature (60 °C), stirring speed (600 rpm) for 40 min in presence of DPE (co-solvent to alcohol molar ratio, 1:1) and was characterized by H^1 NMR and FT-IR analysis. Properties of synthesized biodiesel were determined according to ASTM standards. Reusability of catalyst was checked and the catalyst was found stable up to six runs without any significant loss of catalytic activity.

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1. Introduction

Besides low availability of fossil fuels, their negative impact on environment has compelled the search of eco-friendly renewable alternatives [1]. Over consumption of fossil fuels due to enormous energy demand has led to serious health issues and pollution problems [2]. Air pollution is recorded as major environmental concern as the combustion of fossil fuels results in large scale emission of pollutants. It consists of several hazardous gases along with various sized particulate matter and emission of $PM^{2.5}$ has been increased at an alarming rate [3,4]. Due to their extremely small size, the particles enter into the respiratory tract and cause lung's blockage and are responsible for several respiratory complications. They also hamper the natural phenomenon causing smog and numerous detrimental effects on environment. This has triggered scientific community to seek alternative sources of fossil fuels. Biodiesel is a biologically derived potential alternative of petro diesel [5,6]. Biodiesel is defined as 'mono-alkyl esters of saturated or unsaturated fatty acids' derived from edible and non-edible oils [7]. Biodiesel has additional characteristics than petro-based products such as low emission with low or no sulfur content, no aromatic content, higher biodegradability, higher lubricity, high flashpoint, and high compatibility for compressed engine [8]. Biodiesel is primarily manufactured from vegetable oils in most of the countries. Conventional methods for the use of vegetable oil in CI engine are direct blending and micro emulsion with petrodiesel but it causes problem of carbon accumulation and lube pollution [8]. Thus, biodiesel synthesis using transesterification helps in alleviating the aforesaid issues.

Feedstocks used for biodiesel production comprises of various undesired components alongwith fatty acid esters which make the oil unsuitable for direct use. To overcome this problem, several chemically modified methods are adopted including transesterification, pyrolysis and micro-emulsion. Among these techniques, transesterification is less energy intensive and versatile method to produce biodiesel as renewable fuel. Theoretically, transesterification or alcoholysis is the catalyzed reaction between triglyceride of fatty acids with alcohol [9]. Alcoholysis is quite analogous to hydrolysis where deprotonation of alcohol followed by reversible exchange of triglyceride esters with fatty acid methyl esters (FAME) seems to be the key step. Here catalyst plays crucial role. Basically, transesterification reaction includes the usage of acid, base and enzyme catalyst. Though, homogeneous catalyst results in production at high rate which may be due to ease of interaction between catalyst and alcohol in same phase, but, it leads to higher cost due to implication of costly separation procedure and less regenera-

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tion capability. Conventionally, several homogeneous alkaline catalyst such as NaOH, KOH, CH_3ONa and CH_3OK are employed, where as H_2SO_4 and H_3PO_4 are used as homogeneous acid catalysts [10]. Homogeneous base catalysts are generally used in industries at large scale due to several reasons including capability to catalyze the reaction at relatively low temperature and pressure, economical availability and high conversion rate. Moreover, it is also reported that base catalyzed reactions are 4000 times faster than that of acid catalyzed reaction [11].

Leung and Guo reported biodiesel production from waste frying oil using NaOH as a homogeneous base catalyst as it is cheap and having high reaction rate and yield as well [12]. They obtained 80–90% FAME conversion using 7:1 alcohol to oil molar ratio in 20 min at 60 °C. However, usage of base catalyst carries its limitation of possibility for soap formation [12]. Acid catalyzed transesterification reactions have also been explored by several researchers. Wang et al. [13] reported biodiesel production from waste cooking oil using sulphuric acid as a homogeneous acid catalyst which resulted in FAME conversion of > 90% using 20:1 alcohol to oil molar ratio at 4 wt % catalyst dose in 20 h. As acid and base catalysts have their own merits and demerits regarding transesterification reaction conditions. Hence, both types of catalyst are employed successively in two steps to produce biodiesel from the feedstocks having high free fatty acids (FFA) content. In first step acid catalysts are used to convert free fatty acid to ester through esterification. For base catalyzed transesterification amount of FFA must be lowered to 4 mg KOH/g [13,14].

Considering the point of easy recovery of catalyst via simple solid-liquid separation method, heterogeneous catalyst is supposed to be better for biodiesel production [15,16]. Though, solid catalyst provides aforementioned benefits, but still so many serious flaws need to be tackled during transesterification process as it gets affected by presence of water, high free fatty acid content, requirement of high temperature, and leaching of active metals [17].

Alkaline earth metals are found to be most suitable candidates as solid base catalysts because of their higher basic strength next to alkali metals [18–23]. Basic strength of a metal oxide lies in the presence of $M^{2+}$and O^{2-} ion pairs with different coordination numbers at lattice points assigning a particular geometry. The ions lying at edges having tendency to interact with foreign entity because of unsaturation in bonding at surface, play important role to polarize the CH_3O–H bond to form acyl acceptors [22,24]. As the basic property goes on increasing from top to bottom in the same group, the basic strength of group(II) metal oxides and hydroxides increases in the order of Mg < Ca < Sr < Ba [25,26]. However, if charge density is considered along with basicity, strontium appears to be more effective than any other metal of group (II).

In biodiesel production, deprotonation of alcohol is the key step which controls the overall FAME conversion. Ease of deprotonation is directly related to polarizing power of catalyst species, which depends on charge density. Keeping this theory in mind attempts have been made to utilize the high basic strength and charge density of strontium oxide [27,28] for catalyst synthesis. Further, it was earlier reported that doping with rare earth ameliorates the catalytic activity of base catalyst due to its variable valences [29]. In addition to this, lanthanum oxide has the basic property which is supposed to enhance the total basicity of the catalyst. Various researches have investigated the enhanced catalytic performance of the catalyst after being modified with lanthanum [30]. Therefore, in this study we investigated the potential of Lanthanum doped Strontium oxide for biodiesel production. Both of the metals are non toxic and environmentally benign. Lanthanum oxide does not impart any carcinogenic impact even at dose of 2350 mg direct oral exposure to chlorella species which is supposed to be very sensitive in plant kingdom [31]. In case of strontium oxide only, radioactive isotope Sr^{90} is notorious for causing cancer in body.

The prime step in biodiesel production is the proper selection of feedstock which controls the cost and quality of the product. In present study, Schleichera Oleosa oil has been employed as non edible feedstock for biodiesel production. Predominantly, this feedstock prevails in Indian subcontinent region. This tree found extensively in almost all the parts of India and its annual production was reported as 66 thousand tons per year in India, suggesting that this could be a potential feedstock for biodiesel production [32]. Only few publications on utilization of S. Oleosa oil as feedstock have been reported till date [32,33]. To the best of our knowledge on the basis of meticulous literature review, the application of strontium lanthanum mixed metal oxide for transesterification has never been reported so far.

In present study, Lanthanum doped Strontium oxide as a basic catalyst was synthesized by co-precipitation method, followed by its characterization using various instrumentation techniques such as TGA/DTA, XRD, ATR-FTIR, SEM, EDS, specific surface area and basicity. Further potential of synthesized catalyst was examined for transesterification of S. Oleosa oil for biodiesel production. The factors influencing FAME conversion such as catalyst dose, alcohol to oil molar ratio, time, temperature, stirring, presence of co-solvent, and catalyst reusability were also examined. Moreover, physicochemical properties of the produced biodiesel including calorific value, cetane number, density, flash point, saponification value and viscosity etc. were compared as per ASTM 6751 standards [34].

2. Materials and experimental methods

2.1. Chemicals and raw materials

S. Oleosa seeds were collected from a nearby village area. The chemicals, strontium nitrate, and lanthanum nitrate were procured from Alfa Aeser, U.K. Sulphuric acid, sodium carbonate, deuterated chloroform, sodium sulphate, hexane, acetone, di-isopropyl ether (Merck Millipore, Germany), methanol, toluene, bromothymol blue, methyl red, neutral red phenolphthalein, nile blue and trapeolin and benzoic acid were of analytical grade and purchased from Merck Ltd., Mumbai, India.

2.2. S. Oleosa seeds processing

S.Oleosa oil was extracted from its seeds. The collected seeds were washed with water to remove adhered impurities followed by drying in an oven at 80 °C for 4 h. Further, seeds were de-shelled to take out oil bearing kernels before drying them at 100 °C for 2 h. Dried kernels were crushed and milled into fine powder and was kept in an oven for drying at 50 °C for 3 h.

2.3. Oil extraction

Soxhlet apparatus was used for extraction of oil from the milled kernels using n-hexane as a solvent at 65 °C for 6 h. After extraction of oil, oil–solvent mixture was subjected to evaporation by rotavapor at 68 °C for elimination of solvent from the extracted oil. The composition of the oil in terms of fatty acid content was determined by gas chromatography mass spectra (GCMS).The physical properties such as Iodine value (IV), acid value (AV), density (at R.T.) and kinematic viscosity (at 40 °C) were determined after the oil extraction step according to the ASTM standards. All data reported here are average values of triplicate assays.

2.4. Catalyst synthesis

Co-precipitation route was followed for the synthesis of strontium lanthanum oxide. For catalyst preparation, nitrate precursors of strontium and lanthanum were taken in a definite stoichiometric ratio (Sr/La with molar ratio of 1:2) in distilled water.

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