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A cleaner route of biodiesel production from waste frying oil using novel potassium tin oxide catalyst: A smart liquid-waste management

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ARTICLE INFO

Article history: Received 30 May 2021 Received in revised form 25 August 2021 Accepted 31 August 2021

Keywords: Potassium tin oxide Optimization Reusability Kinetics Green parameters

ABSTRACT

The valorization of waste frying oil (WFO) to biodiesel has been carried out via solid base catalyzed transesterification reaction. A novel potassium tin oxide (KSO) catalyst was synthesized via polymer precursor auto combustion method. The catalyst showed the best physicochemical properties when it was calcined at 800 °C. Using KSO 800 catalyst, the highest FAME conversion (99.5%) of WFO found at moderated reaction condition within very short time (35 min); moreover, no leaching of K-species was observed in reusability test upto 5th cycle. Kinetics proved that the above catalytic reaction followed pseudo-first-order kinetics and the rate of the reaction doubled with increasing 10 °C reaction temperature. The reaction activation energy, enthalpy of activation, entropy of activation, and Gibb's free energy of activation of the reaction were found to be 66.52 kJ/mol, 62.95 kJ/mol, -74.07 J/mol/K and 88 kJ/mol respectively. Evaluation of the green parameters revealed that KSO 800 catalyzed transesterification process approached a cleaner route with excellent efficacy in terms of turnover frequency and yield. KSO 800 helped to produce high quality biodiesel from WFO adopting faster and greener reaction pathway. Thus, KSO 800 was considered as a potential and green catalyst for transforming waste oil into biofuel.

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1. Introduction

Current issues like population explosion, high energy demand, fast depletion of non-renewable energy resources, and the concern for future energy crisis have insisted to explore sustainable resources for continuous energy supply. To stay in control of the global warming limit (2 °C/year) needs serious attention of society for replacing conventional primary energy generation methods (e.g., burning of coal, petroleum, and natural gas) by low-emission alternatives (Mahian et al., 2021). As a supplementary of petrodiesel, biodiesel has been appreciated throughout the world for its compatible physicochemical as well as fuel properties of conventional diesel. Biodiesel is a nontoxic, less polluting, and biodegradable fuel (Verma and Sharma, 2016). Combustion of biodiesel possesses lower CO_2 and CO emissions along with other exhausting gas emissions. Besides, application of biodiesel blends into the existing Compression-Ignition (C.I) engine doesn't require any major modification in engine design (Sajjadi et al., 2016).

Biodiesel is a mixture of monoalkyl esters of saturated or unsaturated fatty acids having carbon number 10 to 22. It is derived from dif-

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https://doi.org/10.1016/j.wasman.2021.08.046 0956-053/© 2021 ferent feedstocks as vegetable oils (like soybean oil, sunflower oil, etc), lignocellulosic biomasses (like Ricinus communis oil, Jatropha curcas oil, etc), algae, waste oils, and animal fats. Cost analysis of biodiesel production estimates that 70% to 80% of total production cost is shared by its feedstock. So, it is very important to choose a potential as well as low cost feedstock for the economic production of biodiesel (Baskar and Aiswarya, 2016; Musa, 2016). Waste frying oil (WFO) should be a more appropriate candidate for the best feedstock as it is easily abundant and cheaper than other feedstocks (Mohammadshirazi et al., 2014, Pugazhendhi et al., 2020). Moreover, the discarded oil creates severe ecological damage in the aquatic environment. The immiscible nature of such waste oils allows creating a layer on to the surface water, which causes lowering the dissolved oxygen level in the aquatic medium. So, it makes difficult for microbial organisms to oxidize the hydrocarbons present in the system, which in consequence, seriously affects the ecology of the water body (Khan et al., 2007; Pikula et al., 2019). In addition, the carcinogenic and mutagenic nature of such discarded oil is equally harmful for human beings (Gurbuz and Ozkan, 2019). Therefore, the use of waste oil or WFO to biodiesel should be admired for waste to well transformation. Food Safety and Standards Authority of India (FSSAI) has published a report that India is the largest consumer of edible oil or vegetable oil, imports 225 lack tones per year. 30% of total consumed oil has been discarded as waste oil due to quality issues. According to India's biodiesel policy, it is declared that India will recover approx 220 Cr lit waste oil to produce biodiesel (Roy et al., 2020a). So, we must say that in India, waste frying oil has a large potential to be a sustainable resource for biodiesel production.

Biodiesel can be produced by various techniques as dilution, pyrolysis, microemulsion, and transesterification. But among all these processes, transesterification is simpler, economic, and more reliable (Meher et al., 2006). In the transesterification process, two important components are required for converting triglyceride (feedstock) to alkyl ester of fatty acid (biodiesel); these are alcohol and catalyst. Generally, methanol and ethanol are used as alcohol in the transesterification reaction. But methanol is extensively used because of its easy abundance and cost-effectiveness (Shahani et al., 2019). The product biodiesel derived by using methanol as alcohol is the mixture of fatty acid methyl ester or FAME. Next, the catalyst is one of the most important components in transesterification as it pushes the reaction to achieve the ultimate goal by adopting the lower activation energy pathway (Nagm et al. 2019). Basically, three types of catalysts like homogeneous, heterogeneous, and enzymatic catalysts are used in the transesterification process. Till now, in industry level biodiesel production homogeneous catalysts like NaOH, KOH, H₂SO₄, NaOCH₃, etc are deployed as they all are cheap and efficient, though it produces a large amount of wastewater in purification step (Borges and Díaz, 2012). Moreover, such corrosive homogeneous catalysts also disturb the environmental diversity. Enzymatic catalysts possess low reaction rate and poor reproducibility. Additionally, this type of catalyst is costly and very sensitive compare to others (Gog et al., 2012). However, heterogeneous catalysis is more advantageous over homogeneous and enzymatic catalyst, as it neither demands any additional purification for catalyst separation nor intensive care for preventing any type of contamination. Moreover, it can be used several times with good efficiency. So, from the commercial point of view, the synthesis of an efficient heterogeneous catalyst is much profitable for biodiesel production (Georgogianni et al., 2009).

Supported heterogeneous catalysts are well known for their immense activity and reusability in the transesterification reaction. Some of these good supported materials are Al₂O₃ (Xie and Li, 2006), SiO₂ (Xie et al., 2015), TiO₂ (Alsharifi et al., 2017), zeolites (Fereidooni et al., 2021a; Fereidooni, et al. 2021b), SnO2 (Wang et al., 2004), etc. providing large surface area, better stability, and long durability of the catalyst. Among these aforementioned materials, former four have been already studied thoroughly in the field of biodiesel production but the last one i.e. tin oxide (SnO₂) is reported by very few researchers. Reviewing such reports, it has been found that SnO2 is suitable as a supporting component for both acidic and basic heterogeneous catalysts. Some of the best tin oxide supported acid catalysts are: SnO₂-SiO₂ reported by Xie et al., (2011), showed 81.7% conversion of soybean oil in moderated reaction condition. Another one is a super-acid catalyst (sulfated tin oxide) reported by Lam et al. (2009), endorsed high efficiency of 92.3% yield in transesterification of high FFA content waste frying oil. Likewise, some best examples of SnO2 supported base catalysts are also discussed as follows. Xie and Zhao (2013) investigated the activity of calcium supported tin oxide as a heterogeneous base catalyst in the transesterification reaction. The catalyst having Ca : Sn equals to 4: 1 showed the best performance of 83.9% oil conversion. Roy et al. (2020a) researched the efficacy of barium stannate as a single phased solid base catalyst, which revealed remarkable efficiency within a very short time; moreover, it also found that the catalytic process is environmentally benign up to three cycles. Both acid and base solid catalysts show good result in biodiesel synthesis but the former one has associated with several issues. The acidic catalysts have short durability and it require comparatively higher temperature to acquire the threshold energy of the reaction; moreover, theses produce a large amount of waste (solvent) (Diamantopoulos et al., 2015). Thus, concerning the environmental causes and economic site of the biodiesel production, it is considered that solid base catalysis is a better option than solid acid

catalysis. Alkali or alkaline metal-supported solid catalysts are the best known as a solid base catalysts. So far many researchers have already found that potassium-supported solid catalysts showed immense activity. K₂O/Al₂O₃, KOH/Al₂O₃, potassium titanate, K modified ZnO, K₂CO₃/Al₂O₃, etc are the best examples of high performing K based solid catalyst (Santoso et al., 2019; Ma et al., 2015; Salinas et al., 2016; Yadav et al., 2017). However, above mentioned catalysts suffer some major issues like leaching problem, storage problem, long reaction time, low stability, poor recyclability, etc. In this present work, to counter these problems we were focused to develop a new catalyst which should be stable, efficient, reusable and leaching proof. Primarily it was anticipated that the combination of potassium species with tin oxide may fulfill our expectations. So, our prime aim was to synthesize the novel potassium tin oxide catalyst and investigate its activity in transesterification reaction of WFO. Next was characterization of catalyst in details by the help of TGA-DTA, XRD, XPS, BET-analyzer, SEM-EDAX, and Hammett indicator-titration method. Then characterization of the product biodiesel was carried out by NMR and GC-FID. Aftermath, the influential parameters related to the WFO transesterification were optimized to know the best reaction condition for acquiring the highest catalytic efficacy. Additionally, thermo-kinetic parameters were evaluated to get the every minute information regarding the transesterification process, reusability of the catalyst was assessed, and at last but not the least, the green parameter study of the process was executed to ascertain the cleanness of the reaction pathway. The cleaner, greener and faster approach for biodiesel production using the novel heterogeneous base catalyst was the ultimate aim as well as novelty of this present work.

2. Experimental

2.1. Chemicals and feedstock

Tin (IV) chloride pentahydrate (98%, Sigma Aldrich), potassium nitrate (ACS reagent \geq 99.9%, Sigma Aldrich), citric acid (99%; Alfa Aesar), activated carbon and potassium hydroxide (98%, Merck) were purchased from Advance Scientific (Varanasi, India). Solvents like ammonium hydroxide (ACS reagent 25%), methanol, ethanol, acetone; acid like sulphuric acid, benzoic acid; Hammett indicators as bromothymol blue, nile blue, phenolphthalein, 2,4 dinitro aniline, 4 nitro aniline were all procured from Sigma Aldrich Ltd, U.S. All reagents were used straight to purpose without any distillation or purification. The most important ingredient, waste frying oil (WFO) was collected from IIT Cafeteria, hostel canteens, hostel mess and restaurants nearby IIT BHU campus. The report of physicochemical analysis of this collected waste frying oil has been enclosed as Table S1 (see supporting information).

2.2. Catalyst preparation

The catalyst potassium tin oxide was synthesized in two steps following polymer precursor - auto combustion method (Sahani et al., 2020). In first step, tin hydroxide (Sn(OH)₂) was prepared by coprecipitation method. A solution was prepared by dissolving 10 g of SnCl₄·H₂O5H₂O in 100 ml deionized water (DI). Then, precipitation of Sn(OH)₂ was carried out by adding dropwise 25% ammonium hydroxide into tin chloride solution with the help of a burette under continuous stirring. Ammonium hydroxide was added till the pH value of the solution rose between 8 and 9 which is optimum pH for complete precipitation process of Sn(OH)₂. The precipitate was separated from the mother liquor after aging at room temperature for a day. Then Sn(OH)₂ precipitate was washed for several times by D.I water to remove the unwanted chloride ions followed by drying for 8 h at 100 °C (Roy et al., 2020a). A portion of dried Sn(OH)₂ was calcined at 800 °C for 5 h to get the SnO₂ phase for comparative study.

Potassium-tin oxide (KSO) was then synthesized in next step as follows. First a saturated solution of potassium nitrated was prepared by dissolving 2.628 g of KNO₃ in stipulated amount of water. Then it was poured into ultrasonicated aqueous suspension of Sn(OH)2 and stirred for 30 min. K : Sn atomic ratio was maintained as 2:1. Previously prepared aqueous citric acid solution (7.5 g in 20 ml D.I water) was gradually added to the precursor solution with constant stirring at 65 °C. Here the citric acid was used as complexing agent as well as fuel for the combustion process and it was taken in equimolar concentration of K and Sn. Thereafter, 25% ammonia solution was added dropwise to the reaction mixture to adjust the pH of the medium 7 that was essential for stabilizing the nitrate-citrate complex (Deganello et al., 2009). Then the resultant solution was heated at 110 °C on a hot plate with continuous stirring at a speeding rate of 400 rpm. At that time, water was continuously evaporated from the reaction mixture which was subsequently turned into dense mixture. After 2 h of constant heating, the solution mixture became a polymeric (gel) form. Then the resultant gel was fired at 300 °C (Roy et al., 2020b). During combustion process the carbonaceous product (i.e. citrate- nitrate complex) was burned with bright yellow flint and volatilized to CO₂, whereas, nitrates converted to native oxides of their respective metals. But a small portion of carbon was still present even after completion the combustion process due to incomplete oxidation. The product was obtained in form of black floppy residue considered as crude catalyst. Aftermath, the crude catalyst was calcined at four different temperatures as 500, 600, 700 and 800 °C (with heating rate 10 °C/min) in an air muffle furnace for 5 h (holding time). According to their calcination temperature the activated catalysts were entitled as KSO 500, KSO 600, KSO 700 and KSO 800.

2.3. Characterizations

Prepared catalyst samples and synthesized biodiesel were characterized by various technical methods to ascertain the physicochemical properties. The instrumental specifications and technical details are given in Table S2 (see supporting information).

2.4. Lab scale biodiesel production via transesterification

Initially, the collected WFO was filtered to eliminate the waste suspended food particles. During frying the food stuff, moisture contamination was incorporated into the WFO which might cause hydrolysis of triglyceride molecule present in oil. So, such moisture content was lessened by heating at 80 °C for 3 h. But to complete removal of moisture, a definite amount of activated carbon was added into WFO and agitated at 70 °C for 1 h. Next, free fatty acid (FFA) content of the dried WFO was estimated by acid-base titration method and obtained within the permissible range i.e. < 3 mg KOH/g (ASTM 6751). This implied that WFO could sustain for direct use without any pretreatment process. So, the feedstock was straight to feed into the transesterification process (Yadav and Sharma, 2019).

Lab scale biodiesel production was operated in a temperature controlled batch reactor. The methyl esterification or transesterification reaction was executed in a 250 ml capacity of three necked round bottom (R.B) flask assembled with a reflux condenser, rotation controlled mechanical stirrer and a thermometer. A required amount of catalyst was first dispersed into a definite amount of methanol for the desire reaction in the R.B submerged into the water bath at room temperature for 15 min. Then maintaining oil to methanol molar ratio, a calculated amount of WFO was poured into the flask and stirred at optimum temperature for optimum reaction duration under reflux condition. The important reaction parameters as catalyst activation temperature, oil to methanol molar ratio, catalyst weight %, reaction temperature and time were optimized along with catalyst endurance by following the aforementioned reaction procedure. After carried out the reaction, the product mixture was move to a separating funnel. A day after, the product mixture got settled down and separated in three distinct phases according to their density. Bottom layer was the solid catalyst, middle layer contained glycerol and the upper layer was constituted by FAME or biodiesel and excess methanol. Thereafter, three phases were brought out one by one. Catalyst was washed subsequently by methanol and ethanol and reused in 2nd cycle, whereas byproduct glycerol was stored to use in value-added product synthesis. The synthesized biodiesel was kept in air oven at 65–70 °C for 1 day to rid of the excess methanol present in FAME. Then the product FAME was characterized, quantified and stored for emission test. All the experiments regarding optimization, kinetics and catalyst endurance test were carried out for three times and considered the average as final experimental result.

The quantitative analysis in terms of FAME conversion was accounted by ¹H NMR technique using the following equation (Birla et al., 2012):

$$FAME conversion(\%) = \frac{2A_{OCH_3}}{3A_{\alpha - CH_2}} \times 100$$
(1)

In equation (1), A_{OCH_3} defines the integration of signal associated with the methoxy hydrogen and $A_{\alpha-CH_2}$ ascertains the integration of the signal associated with the α -methylene hydrogen.

3. Results and discussion

3.1. Catalyst characterizations

3.1.1. Thermogravimetric (TG) analysis

The thermal decomposition process of crude potassium stannate catalyst analyzed by TGA-DTA, has been shown in Fig. 1. As can be observed, an initial degradation of 13.54% below 164 °C, which was accompanied by three endothermic events, could be relevant for the elimination of adsorbed water and lattice water. Between 184.4 °C and 470 °C, another mass loss of 5.83% might be resulted due to decomposition of nitrates and citrate. This disintegration was accompanied by formation of metal oxides (SnO₂, KO₂) and metal carbonate (K₂CO₃). Moreover, this process followed an exothermic pathway, was indicated at 427.6 °C in DTA profile. After 480 °C, mass loss process was occurred in a slow and continuous manner upto 737.4 °C. This was happened due to elimination of carbonates (CO₃²⁻) confirmed from the XRD analysis. Beyond 737.4 °C, a sharp degradation in TGA profile was observed between 738 °C and 791.7 °C. This was accompanied by an endothermic event (found at 771 °C in DTA) of phase transformation i.e. individual metal oxide (SnO₂, KO₂) phases to compound mixed metal oxide phases



Fig. 1. TGA-DTA of uncalcined potassium tin oxide.

of potassium stannate (Stambolova et al., 2004). This was also confirmed by XRD analysis. After 791.7 °C, the catalyst got the thermal stability up 846.3 °C. However, above 846.3 °C, K species started to vaporize by an endothermic process indicated at 1114.5 °C in DTA. So, it was expected that the catalyst would show the best efficacy when it was activated between calcination temperature range 791.7–846.3 °C.

3.1.2. Powder X-Ray diffraction (PXRD) study

The crystalline phase along with cell parameters of respective lattice arrangement of different KSO sample varying calcination temperature and time was investigated by powder X-Ray diffraction technique. The appeared peaks for a particular crystalline phase, present in diffractogram were confirmed by the help of JCPDS (Joint Committee of powder X-ray diffraction standards) database. Fig. 2 depicts the diffractogram of respective KSO catalysts with different calcination temperature (500,600,700 and 800 °C). The diffractogram of KSO 500, KSO 600 and KSO 700 were found to have similar peak pattern; whereas, KSO 800 has different peaks. Thus, it can be assured that KSO 500, KSO 600 and KSO 700 were possessed same crystalline phase but KSO 800 had different phases. Fig. S1 (supporting information) shows the characteristic peaks present in KSO 700 and KSO 800 diffractogram. The prominent peaks present in KSO 700 (see Fig. S1A; supporting information) at the following peak position as, $2\theta = 26.6 (1 \ 1 \ 0)$, 33.9 (1 0 1), 37.9 (2 0 0), 51.8 (2 1 1), 54.8 (2 2 0), 57.8 (0 0 2), 61.9 (3 1 0), 64.7 (1 1 2), 65.9 (3 0 1), 69.2 (3 1 1), 71.3 (2 0 2), 78.7 (3 2 1), 81.1 (4 0 0), 87.2 (3 3 0), 89.8 (3 1 2) were confirmed (JCPDS file no. 880287) the presence of tetragonal primitive SnO₂ lattice. The lower intense peaks corresponding potassium (K) phases have been displayed in the inset of Fig. S1A (supporting information). The lower intensity of such peaks signified that K species had lower concentration in material surface (Yadav et al, 2017). KO2 and K2CO3 were found as component phases of potassium in KSO 700 confirmed by JCPDS file no. 895,957 and 711,466 respectively. Most of the peaks corresponding to the KO₂ were overlapped with the peaks associated to the K₂CO₃ lattice; however the most intensity peak regarding KO2 was obtained at 20 value of 25.8 (1 1 0) along with small characteristic peaks at 45 (3 1 3), 45.5



Fig. 2. XRD of potassium tin oxide catalysts calcined at different temperature (500 $^{\circ}$ C, 600 $^{\circ}$ C, 700 $^{\circ}$ C & 800 $^{\circ}$ C) for 5 h.

(2 0 4). The characteristic peaks of monoclinic K₂CO₃ lattice were found at the following 20 position: 28.7(1 0 2), 29.9 (1 1 2), 31.7 (1 3 0), 32.1 (0 2 2), 32.3 (2 0 0), 38.6 (2 0 2), 39.1 (0 4 1), 38.9 (1 3 2), 40.6 (0 1 3), 41.8 (1 1 3), 42.8 (2 2 2), 48.8 (3 0 0), 49.4 (240), 50.4 (151). Overall it was concluded that the KSO catalysts activated between 500 °C and 700 °C possessed SnO₂, KO₂ and K₂CO₃ crystalline phases. Next, Fig. S1B (supporting information) reveals the crystalline phases present in KSO 800. Three distinct crystalline phases of potassium stannate compound as K₂SnO₃ (# JCPDS file no. 720825), K₂Sn₂O₃ (# JCPDS file no. 720196) and K₂Sn₃O₇ (# JCPDS file no. 170599) were obtained. Carbonates were completely demolished and formed potassium-tin mixed metal oxides when the crude catalyst was calcined at 800 °C for 5 h. This fact was also justified the findings in TGA-DTA analysis. All the characteristic peaks of corresponding potassium stannate compounds have been pointed in Fig. S1B (supporting information). Here also many peaks of different phases were overlapped. Comparing JCPDS database, the peak shifting (± 0.5) as well as change in peak intensity was observed but the most intensity peaks of respective compounds were matched well. The phase transformation of potassium stannate compound during calcination time at 800 °C holding temperature was also examined and represented in Fig. S2 (supporting information). This revealed the interesting facts about the effect of high temperature heat treatment (calcination) duration on chemical phase transformation for potassium stannate. Initially (after 1 h), SnO₂ and K₂O were found as the major phase contribution in KSO catalyst. There was no such significant difference in peak intensities observed even after 2 h, which means the aforesaid phases were still belonged as major catalytic phase. Then, a remarkable change in intensities was noticed after 3 h. The peak intensities corresponding to the SnO₂ and K₂O phases decreased whereas, the assigned peak intensities of potassium stannate phases increased. This implied that concentration of SnO₂ and K₂O phases were going to be degraded, and the concentration of potassium stannate compounds was enhanced with time. This was continued even after 4 h. But after 5 h, the native oxides were completely transformed into KSO compound phase. So, it was confirmed that the desirable potassium stannate phases could be acquired at 800 °C calcination temperature and 5 h holding duration.

3.1.3. X-Photoelectron spectra (XPS) study

The oxidation state of the elements present in KSO 700 and KSO 800 was investigated by XPS technique. The wide XPS spectra of KSO 700 and KSO 800 are represented as Fig. 3A and Fig. 3B. In supporting information, Fig. S3A and Fig. S3B display the 2p spectra of K present in KSO 700 and KSO 800 respectively. The binding energy (BE) of K2p_{3/2} and $K2p_{1/2}$ in XPS of KSO 700 were found at 292.6 eV and 295.4 eV. Spin-orbit components (K2p_{3/2} and K2p_{1/2}) spaced by 2.8 eV confirmed K^{+1} state. However, in XPS of KSO 800 the binding energy of $K2p_{3/2}$ and K2p_{1/2} were obtained at 292.8 eV and 295.6 eV, which also indicated the + 1 oxidation of K. But in comparison, it was found that both component peaks shift small approximate to 0.2 eV towards the higher binding energy. This might probably happen due to transformation of K-O bond to K-O-Sn- bond in KSO 800 (Chen et al., 2018). The 3d spectra of tin (Sn) present in XPS of KSO 700 and KSO 800 are shown in Fig. S4A and Fig. S4B (see supporting information) accordingly. In case of KSO 700 the corresponding BE of $3d_{5/2}$ and $3d_{3/2}$ were found at 486.7 eV and 495.1 eV, spaced by 8.4 eV. This assured that Sn was present in + 4 oxidation state. The XPS fitting graph of Sn $3d_{5/2}$ showed only one best fitted peak at 486.7 eV present (in Fig. S4C; supporting information); this also reassured that only Sn⁴⁺ was present as SnO₂ in KSO 700. Herewith, comparing the 3d spectra of Sn present in XPS of KSO 800 showed slight change in BE of 0.3 eV towards the lower binding energy. This fact might be associated with the transformation of a definite amount of Sn⁴⁺ to Sn²⁺. Similar trend of shift in binding energy was also observed by Szuber et al (2001). The XPS fitting graph of Sn 3d_{5/2} (Fig. S4D; supporting information) showed two peaks corre-



Fig. 3. XPS survey of A) KSO 700 and B) KSO 800.

sponding two oxidation state of Sn present in KSO 800. The peak at lower BE (486 eV) was assigned for Sn^{2+} and the higher BE (486.6 eV) peak was designated to Sn⁴⁺ (Jadhav et al., 2017, Kwoka et al., 2005). Aftermath, the BE associated with the O1s of KSO700 and KSO 800 were found at 530.6 eV and 530.6 eV in Fig. S5A and Fig. S5B (see supporting information) respectively. Here also a lower shift of 0.2 eV in O1s spectra for KSO 800 was noted. This result might corroborate the fact delivered for Sn. Due to transformation of O-Sn⁴⁺ to O-Sn²⁺, with increasing calcination temperature 700 °C to 800 °C, both Sn and O showed lower binding energy shift (Jadhav et al., 2017). The deconvolution of O1s in XPS KSO 700 (Fig. S5C; supporting information) revealed three peaks, one at 530.4 eV was assigned to metal oxide (O^{2-}) , second at 531.1 eV was indexed to superoxide O (O⁻) present in KO₂, and last one at 532.3 eV was assigned to the physically adsorbed O which might come from moisture content present at outer surface of catalyst. In XPS of KSO 800, the deconvolution of O1s (shown in Fig. S5D; see supporting information) also depicted three peaks of three different type of O. The lowest BE peak at 529.8 eV was subjected to the O

of $O-Sn^{2+}$, the middle on at 530.7 eV was designated O of $O-Sn^{4+}$, and the higher one at 531.8 eV was assigned to the chemically adsorbed O on catalyst surface (Wu et al., 2015). Thus, the transformation of tin oxide and potassium oxide to potassium stannate due to increasing calcination temperature 700 °C to 800 °C has been clearly elaborated and cross verified the XRD data by XPS analysis.

3.1.4. Scanning electron microscope (SEM) study and energy dispersive X-Ray (EDAX) analysis

The surface topology of tin oxide and potassium tin oxide catalysts (KSO 700 and KSO 800) was visualized by SEM technique. Fig. 4 depicts the morphological difference in three samples namely pure SnO₂, KSO 700 and KSO 800. Besides, the elemental analysis was carried out by the EDAX technique and has been shown accordingly. It has been clearly seen in Fig. 4A that pure SnO₂ had no particular shape and size; moreover, agglomeration of particles and heterogeneity in size distribution implied the amorphous character of SnO₂. The component phases present in KSO 700 has been displayed in Fig. 4B. Comparing Fig. 4A



Fig. 4. SEM image of A) Pure SnO₂, B) KSO 700 and C) KSO 800*; EDAX micrograph of D) pure SnO₂, E) KSO 700, F) KSO 800 (spectrum 2), G) KSO 800 (spectrum 3), H) KSO 800 (spectrum 4)**. *All the areas / points chosen for EDAX analysis mentioned in corresponding SEM images. **Insets of the EDAX include the atomic weight (%) of existing elements.

and Fig.ure 4B, it can be better understood that how the layer of K species covered the entire SnO₂ surface. Small spherical KO₂ and K₂CO₃ species were irregularly deposited over SnO₂ particles. This was due to the strong philicity of K-O bond of K- species toward the Lewis acidic sites (Sn⁴⁺-O) present on the surface of SnO₂. Fig. 4C shows the surface morphology of catalyst KSO 800 where three different types of particles such as rod-shaped particles, dull shaded amorphous solid of large particles and agglomerated spherical shaped particles were spotted.

The identification of phases present in the sample was carried out by EDAX analysis of a particular area or point (as shown in Fig. 4A, Fig. 4B and Fig. 4C) as required. The EDAX micrograph of such respective areas or points has been introduced as Fig. 4D for pure SnO₂, Fig. 4E for KSO 700, and Fig. 4F, Fig. 4G, Fig. 4H for KSO 800, with atomic weight (%) of elements which describes the possible atomic ratio of the elements and the molecular formula of the existing phases. In the case of pure SnO₂, the obtained atomic weight (%) of O : Sn was around 2 : 1, which suggested that the existing phase was SnO₂. Similarly, in KSO 700 catalyst showed K : Sn atomic ratio around 2 : 1 which was approximately the same ratio that was taken in catalyst preparation. Then the point EDAX of KSO 800 helped to interpret the topology of chemically different potassium stannate phases i.e. rod shaped particles were of K₂SnO₃, large sized particles were of K₂Sn₃O₇, and agglomerated spherical particles were of K₂Sn₂O₃. Such EDAX data was also perspicuously supported the facts explained earlier in XRD and XPS analysis.

3.1.5. BET surface area analysis and basic strength analysis

The solid-base catalyzed transesterification reaction is driven by two physicochemical properties of catalyst; one is surface area and the other is basic strength. Basically, the process is synergistically actuated by both the aforementioned factors. The change in surface property due to increase in calcination temperature of potassium stannate catalysts have been comprised in Table 1. Pore size of all KSO catalysts were obtained in the range of mesoporous material (2–50 nm). KSO 500, KSO 600 and KSO 700 possessed lower surface area, however, a slight increase was observed with increasing calcination temperature. KSO 800 showed the highest surface area among all the potassium stannate compounds. These facts are explained with the help of XRD and SEM analysis. Previously we found in XRD that the peak intensities associated with carbonates were reduced according to enhance calcination temperature from 500 °C to 700 °C, and it was completely demolished at

Table 1

Surface	prop	erties	of	potassium	tin	oxide.	
Jurnero	Prop	or croo	~	pottoortuni		on a con	

Name of the sample	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)
KSO 500	0.86	0.0047	18.34
KSO 600	1.78	0.0066	23.94
KSO 700	5.65	0.0094	28.56
KSO 800	32.04	0.0558	15.09

800 °C. The SEM image of KSO 700 reveals that carbonates were heterogeneous accumulated on to the SnO2 surface, which is the definite cause in surface area reduction. As the concentration of carbonate species decreased with increasing calcination temperature, in consequence, the surface area of catalysts increased accordingly. KSO 800 is composed of carbonate-free pure potassium stannate compounds, which was morphologically better compared to others. Thus it showed best result in BET surface area analysis. Next, basic strength of the catalysts was measured by Hammett indication benzoic acid titration method (Yadav and Sharma, 2019; Sahani et al., 2020; Naveenkumar and Baskar, 2020). The basicity of KSO 500, KSO 600, KSO 700 and KSO 800 were found to be 0.74 mmol/g, 0.97 mmol/g, 1.21 mmol/g and 1.76 mmol/g respectively. Here also we observed that basicity was improved with enhancing calcination temperature. Basically, carbonate (CO_3^{2-}) is acidic in nature and it usually clogged the basic active sites to interact. So, at higher temperature carbonates were removed from the basic sites of the catalyst surface with improvising the basicity strength property (Sahani et al. 2019). Thus, KSO 800 demonstrated the best result in Hammett indicator test because of there was no carbonate species inside it. So, considering surface properties and basicity, KSO 800 is approved as the best catalyst among other KSO catalysts for biodiesel production from WFO through transesterification process.

3.2. One variable at a time (OVAT) optimization of reaction parameters

In literature it is reported that the parameters namely catalyst activation (calcination) temperature, calcination time, oil to methanol molar ratio, catalyst weight percentage, reaction temperature and time have significant contribution in transesterification reaction. So, these above mentioned parameters need to optimize for achieving the best result in terms of FAME conversion (%). Conventional OVAT methodology was followed for such optimization process.

3.2.1. Optimization of catalyst activation temperature and time

Fig. 5A demonstrates the effect of different catalyst activation (calcination) temperature on FAME conversion of WFO. The catalytic efficacy of KSO catalysts activated at 500 °C, 600 °C, 700 °C, 800 °C and 900 °C were investigated under the following reaction condition: 1:16 oil to methanol molar ratio, 2.5 wt% of catalyst weight, 65 °C reaction temperature, 35 min reaction duration. This study shows that rising the catalyst activation temperature actually improves the catalytic efficiency. The KSO catalyst showed highest activity while it was activated at 800 °C; however, above 800 °C, activity of this KSO catalyst was reduced. This observation can be explained by correlating the results of XRD, BET and basicity analysis. In XRD, we found the carbonates were present in KSO catalysts activated at the temperature below 800 °C, but the concentration of such carbonate species subsequently decreased with increasing the catalyst activation temperature and completely exhausted at 800 °C. With the removal of carbonate species,



Fig. 5. Activity of potassium tin oxide catalyst A) calcined at different temperature B) calcined for different duration at 800 °C.

two most important properties of KSO catalyst i.e. BET surface area and basicity simultaneously were increased, which in consequence improved the catalytic activity. KSO 800 possessed the best conversion because of its highest BET surface area and higher basicity. Beyond 800 °C the active component of the catalyst i.e. the potassium species started to decompose, as a result, FAME conversion (%) was affected and became decreased. Next, the effect of activation time on FAME conversion (%) has been shown in Fig. 5B. The catalyst KSO 800 was activated at different times, such as 1 h, 2 h, 3 h, 4 h, 5 h & 6 h. It was observed that FAME conversion (%) of WFO was improved with the increment in the calcination period up to 5 h and then it became constant. This might be happened probably due to phase transformation of native oxides of Sn and K to potassium stannate. In XRD analysis, we noticed that concentration of tin oxide and potassium dioxide decreased with increasing calcination duration, whereas, concentration of potassium stannate phases increased with time. The particles of KSO 800 catalyst calcined for 5 h, showed good surface topology in SEM analysis; moreover, it also possessed high surface area and basicity. So, in transesterification the best result of KSO 800 was found while it was activated at 800 °C for 5 h duration.

3.2.2. Optimization of oil to methanol molar ratio and catalyst weight percentage

Fig. 6A depicts the influence of oil to methanol molar ratio on FAME conversion (%) of WFO. Lee Chateleir's principle states that for a reversible reaction the equilibrium shifts toward that direction where stress may possibly release. As we all know that transesterification reaction steps are reversible, so it needs alcohol (methanol) in excess amount than the stoichiometric amount (1 : 3) defined in balanced equation. Such excess methanol evolves stress at the reactant side, which relieves from the product methyl ester side, and helps to shift

the reaction equilibrium to the forward direction (Leclercq et al., 2001). In this study, the optimum oil to methanol molar ratio was obtained at 1:16; which is higher than 1:3, and also well justified by the above mentioned aspect. Initially, the increment in methanol concentration promoted the methanolysis reaction which in consequence favored the biodiesel conversion. As soon as the requirement of methanol was fulfilled, the reaction proceeded immediately. At 1:16 oil to methanol molar ratio, the reaction achieved the most favored condition where the equilibrium was shifted to the product side at maximum extent. However, beyond 1: 16 M ratio, by product glycerol started to dissolve in excess methanol; thus the equilibrium was disturbed and reaction got disfavored again (Singh et al., 2016a). As a result FAME conversion (%) was lowered as shown in optimization plot (Fig. 6A). Next, the catalyst weight percentage was optimized for WFO transesterification (shown in Fig. 6B). In heterogeneous catalysis, catalyst plays the most important character to precede the reaction. The chemical reaction can only occur in active sites present at surface of the catalyst. This means the number of available active site depends only on the concentration or the weight (%) of the catalyst present in reaction. So, it is interpreted that increased catalyst weight (%) introduces the larger number of active sites, which possibly reinforces the FAME conversion (Sahani et al., 2019). Fig. 6B manifests that the transesterification reaction of WFO using KSO 800 catalyst was accelerated to the maximum extent in presence of 3 wt% catalyst concentration. But higher than 3 wt% catalyst weight, this reaction was obstructed because of enhancing fluid viscosity in the reaction medium (Singh et al., 2016b). Moreover, the mass transfer between three phases severely disrupted in viscose media which has been evidentially shown in optimization plot as reduction in FAME conversion at high concentration of catalyst (i.e. 4 wt%).



Fig. 6. Optimization of A) oil to methanol molar ratio (reaction conditions: catalyst weight -3 wt%, temperature -65 °C, time -35 min), B) catalyst weight percentage (reaction conditions: oil to methanol molar ratio 1:16, temperature -65 °C, time -35 min), C) reaction temperature (reaction conditions: : oil to methanol molar ratio 1:16, catalyst weight -3 wt%, time -35 min), & D) time (reaction conditions: oil to methanol molar ratio 1:16, catalyst weight -3 wt%, temperature -65 °C).

3.2.3. Optimization of reaction temperature and time

For any chemical reaction two key parameters such as reaction temperature and time govern the kinetics of the process. The influence of temperature on FAME conversion (%) of WFO was investigated by executing numerous batch reactions over a temperature range starting from room temperature to 75 °C. These batch reactions were carried out under following reaction condition: 1:16 oil to methanol molar ratio, 3 wt% catalyst weight, 45 °C-75 °C temperature with 5 °C interval, and 35 min duration. The resultant data has been presented in Fig. 6C which depicts that FAME conversion was improved with increasing reaction temperature 45 °C to 65° but decreased above 65 °C. Therefore, the optimized reaction temperature of this transesterification process was considered to be 65 °C which was close to boiling point (BP) of methanol. At this optimum temperature, the system acquired the external energy required to come across the threshold barrier for preceding the reaction towards forward direction. Moreover, the acyl acceptor produced from methanol was fully activated at this temperature to interact with the triglyceride molecule to form FAME or biodiesel with the best result (Yadav et al., 2017). However, at the temperature above 65 °C methanol started to vaporize and lost in significant amount from the triphasic reaction mixture. Thus, the FAME conversion was reduced subsequently with increase in reaction temperature above the optimum value (Roy et al, 2020c; Putra et al., 2018). Next, the second most important parameter for a kinetic reaction is reaction duration or time. The time of this transesterification process was optimized by extending the reaction for 1 h under the following reaction condition: 1:16 oil to methanol molar ratio, 3 wt% catalyst weight, 65 °C reaction temperature. The optimum time of the process was ascertained in terms of highest FAME conversion (%). Fig. 6D displays that the more than 90% methyl ester was formed within 15 min and completed in 35 min. The effect of time on FAME conversion can be elaborated by corroborating the above result with the previous studies. Initially, the reaction was diffusion controlled; so, it was unable to produce a significant amount of methyl ester in 5 min. But whenever the reaction became kinetically controlled, a sharp amplification in FAME conversion was observed in time profile. Due time, the reaction approached the equilibrium and became slow down (Balat and Balat, 2010). Around 35 min, the reaction got the equilibrium phase. So, it can be interpreted that the above mentioned reaction has completed in 35 min. Beyond that optimum time, It is assumed that FAME conversion was deducted due to promotion of backward reaction i.e. hydrolysis of methyl ester (Singh et al. 2016b).

3.3. Kinetics and thermodynamics

3.3.1. Evaluation of rate constant at various temperature

The balanced equation of transesterification reaction is written below:

$$\begin{aligned} Triglyceride + 3MeOH \leftrightarrow 3Fattyacidmethylester \\ + glycerol \end{aligned} \tag{2}$$

The above equation (2) derives that rate of the reaction depend on both concentrations of triglyceride or oil and methanol. As we take methanol in much excess (1 : 16) than the stoichiometric amount (1 : 3), we may assume that change in methanol concentration will be negligible. So, according to this pre-assumption we can write the rate equation as follows:

Rateofthereaction =
$$\frac{d[Tg]}{dt} = k[Tg]$$
 (3)

where, $\frac{d[Tg]}{dt}$ is the change in concentration of triglyceride per time (t in min), [Tg] is the concentration of triglyceride and k is rate constant for the reaction.

Now, the mass balance equation is

$$x_{FAME} = 1 - \left(\frac{\left[Tg\right]_{t}}{\left[Tg\right]_{0}}\right) \tag{4}$$

$$\therefore [Tg]_t = [Tg]_0 (1 - x_{FAME}) \tag{5}$$

Here, x_{EAME} refers the FAME conversion, $[Tg]_t \& [Tg]_0$ define the concentrations of triglyceride at time t and at time 0 respectively.

Integrating the equation (5):

$$-\ln\left(1 - x_{FAME}\right) = k \times t \tag{6}$$

Thus, rate of the reaction can be determined by calculating the slope of the plot $-\ln(1 - x_{FAME})$ vs t (in min) (Encinar et al., 2018). Then, the batch reactions were performed at three different temperatures (45 °C, 55 °C, & 65 °C) under optimized oil to methanol molar ratio (1 : 16) & catalyst weight (3 wt%) for 35 min. Over the duration range of 5 to 35 min, after every 5 min interval methyl ester conversion was analyzed. Then the resultant data was plotted following the above equation (6). The Fig. 7A represents the kinetic plot of the transesterification of WFO using KSO 800 catalyst. The R² values of three distinct linear plots at 45 °C, 55 °C, & 65 °C were found to be 0.966, 0.982, & 0.994 respectively. This result approves that our pre-assumptions are completely right; the rate of the reaction only depends on triglyceride concentration; moreover, it also proves that the aforementioned reaction is a pseudo first order reaction. The corresponding rate of the reaction at temperature 45 °C, 55 °C, & 65 °C were determined to be 0.0432 min⁻¹, 0.0818 min⁻¹, & 0.1457 min⁻¹. This implies that reaction rate was enhanced around 2 fold after raising 10 °C reaction temperature.

3.3.2. Evaluation of activation energy

According to the Arrhenius equation,

$$k = A\exp(-\frac{E_a}{RT}) \tag{7}$$

or,
$$lnk = lnA - E_a/RT$$
[takinglogofeq.7] (8)

Here in equation (8), A is the frequency factor (min⁻¹), E_a is the threshold energy or activation energy (J/mol), R is universal gas constant (value 8.314 J/K/mol), & T is Kelvin temperature. Following this above equation, a linear plot of l_{nk} vs 1/T was drawn to find out reaction activation energy as shown in Fig. 7B (Chen et al., 2020). From the slope (E_a/RT) of this linear plot, activation energy of the transesterification of WFO using KSO 800 catalyst was calculated to be 66.52 kJ/mol which exhibited in the range for basic heterogeneous catalysis (i.e. 33.6–84 kJ/mol). The frequency factor A was calculated to be 34.1×10⁸ min⁻¹ from the intercept (l_{nk}) of the same plot. Basically, frequency factor impacts on the reaction duration. In our case, the reaction has completed comparatively in short time (35 min) due to high frequency factor.

3.3.3. Evaluation of thermodynamic parameters

Eyring- Polanyi's equation leads to

$$k = \frac{k_b T}{h} \times \exp\left(-\frac{\Delta G^{\#}}{RT}\right) \tag{9}$$

In equation (9), k_b is the Boltzmann constant (value 1.38×10⁻³⁸ J/K), h is Plank constant (value 6.626×10⁻³⁴ J.s, $\Delta G^{\#}$ is Gibb's free energy of activation.

Now compiling the Eyring- Polanyi's equation with the fundamental equation of thermodynamic we get,

$$k = \frac{k_b T}{h} \times \exp\{-\frac{(\Delta H^{\#} - T\Delta S^{\#})}{RT}\} \left[as \Delta G^{\#} - \Delta S^{\#} \right]$$

$$= \Delta H^{\#} - T\Delta S^{\#}$$
(10)



Fig. 7. Thermo-Kinetic plots of transesterification reaction of WFO catalyzed by KSO 800; A) Kinetic plot (-ln(1-ME) vs t), B) Arrhenius plot (lnk vs 1/T), C) Eyring-Polanyi's plot (ln(k/T) vs 1/T).

or,
$$\frac{k}{T} = \frac{k_b}{h} \times \exp\left(\frac{-\Delta H^{\#} + T\Delta S^{\#}}{RT}\right) \left[\Delta H^{\#} - \text{enthalpyofactivation}, \Delta S^{\#} - \text{entropyofactivation}\right]$$
(11)

Taking log of eq. (11),

$$\ln\left(\frac{k}{T}\right) = \left[\ln\left(\frac{k_b}{h}\right) + \left(\frac{\Delta S^{\#}}{R}\right)\right] - \left(\frac{\Delta H^{\#}}{RT}\right)$$
(12)

Following the above equation (12), we plottedln($\frac{k}{T}$)against 1/T as shown in Fig. 7C. Enthalpy of activation($\Delta H^{\#}$) and entropy of activation ($\Delta S^{\#}$) were calculated respectively from the slope (i.e. $\Delta H^{\#}/R$) and the intercept (i.e. $\ln\left(\frac{k_h}{h}\right) + \frac{\Delta S^{\#}}{R}$) of the aforesaid linear plot (Galvan et al. (2013). The resultant values of $\Delta H^{\#}$ and $\Delta S^{\#}$ were found to be 62.95 kJ/mol and -74.07 J/mol/K for the given transesterification process. Positive sign of $\Delta H^{\#}$ and negative sign of $\Delta S^{\#}$ signify that the process follows endothermic pathway and during the reaction, entropy of the system will decrease. Next, $\Delta G^{\#}$ was determined by using the fundamental equation of thermodynamic and it was found 88 kJ/mol. These results are good agreement with the results reported by Galvan et al. (2013) and Yadav and Sharma (2019).

3.4. Mechanism of transesterification reaction using KSO 800 catalyst

The mechanistic pathway of methyl esterification reaction of WFO using KSO 800 as a solid base catalyst is designed on the basis of the literature survey (Aransiola et al., 2014; Tapanes et al., 2008). There are three component phases i.e. $K_2Sn_2O_3$, K_2SnO_3 , and $K_2Sn_3O_7$ are present in KSO 800 catalyst, which was confirmed by XRD analysis. These all three phases are considered to be the active phase as all have the same functional groups in their molecular structure. The catalytic routes of $K_2Sn_2O_3$, $K_2Sn_2O_3$, $K_2Sn_3O_7$ and $K_2Sn_3O_7$ and $K_2Sn_3O_7$ and $K_2Sn_3O_7$ and $K_2Sn_2O_3$ have been depicted in Fig. 8. These cat-

alytic pathways follow a cyclic process which is constructed by three crucial steps: adsorption, chemical reaction, & desorption. In step I, triglyceride and methanol adsorbed to the active sites present on the catalyst surface. The K-O bond in KSO 800 catalyst acts as the basic active site where triglyceride has physically adsorbed and methanol has chemically adsorbed. As soon as methanol adsorbed to the active site, it becomes dissociates and forms methoxide ion (CH₃O⁻). Then in step II (i.e. surface reaction), the methoxide ion acts as a nucleophile that approaches the electrophilic site i.e. carbonyl carbon of adsorbed triglyceride molecule. Herewith, a rearrangement reaction proceeds through a tetrahedral intermediate formation which subsequently transformed to diglyceride and released one molecule of fatty acid methyl ester (FAME) (Demirbas, 2008). In the final step, the deprotonated diglyceride molecule acquires a proton from the protonated catalyst and desorbed from the catalyst surface (Guo et al., 2012). Thereafter, the free catalyst will get into another cycle where it may interact with triglyceride or diglyceride, or monoglyceride, however, the mode of interaction will be the same as before. At the end of the process, it will produce glycerol and a mixture of fatty acid methyl ester.

3.5. Characterization of biodiesel by ¹H NMR and ¹³C NMR

The product of transesterification of WFO was characterized by NMR spectroscopy. The chemical nature of the product was confirmed by comparing the respective spectra of feedstock and the product. ¹H NMR and ¹³C NMR spectra of the product are displayed in Fig. S6A and Fig. S6B (see supporting information) respectively; however, Fig. S7A and Fig. S7B (in supporting information) represent the ¹H NMR and ¹³C NMR spectra of feedstock respectively. In¹H NMR spectra of product, the following characteristic peaks were noticed at 5.38–5.28 ppm assigned for multiplet –CH = CH proton, 3.64 ppm assigned for singlet –OCH₃ proton, 2.76–2.74 ppm assigned for triplet C = C-CH₂-C = C proton, 2.30–2.27 assigned for triplet –OCO-CH₂ (α -methylene) proton, 2.05–1.97 ppm assigned for multiplet –CH₂-C = C proton, 1.61–1.57 ppm assigned for multiplet –CH₂-C = O proton,



Fig. 8. Mechanism of transesterification reaction of WFO using KSO 800.

1.36-0.94 ppm assigned for -CH₂, 0.88-0.85 ppm assigned for CH₃ (Ba et al., 2016). These characteristic peaks were also found in ¹H NMR spectra of WFO; this suggested that same backbone was present in oil and the product. However, the multiplet signals found in case of WFO at 4.33-4.30 ppm and 4.18-4.14 ppm assigned for glyceride protons, were completely demolished after transesterification as it was found almost nil in ¹H NMR spectra of product. In addition, the signal regarding methyl ester proton was profoundly ascertained in product. These particular suggested that triglyceride moiety might be substituted by methoxy group and formed long chain fatty acid methyl ester, i.e. FAME or biodiesel (Roy et al., 2020b). This was cross-verified by ¹³C NMR spectral analysis. In case of oil, the signals of ¹³C NMR was recorded at chemical shift value to be 172.8-173.3 ppm designated for three-C = O (carbonyl) carbons, 131.9-127 ppm assigned for -CH = CH (olefinic) carbons, 77 ppm assigned for solvent CDCl₃ carbon, 68.9 ppm & 62.1 ppm assigned for CHO & CH₂O (glyceride backbone) carbons, 34-22.6 ppm corresponds to -CH₂ (methylene) carbons, 14 ppm assigned for -CH₃ (methyl) carbon. In product three signals of carbonyl carbons converted to single carbonyl signal was found at 174.3 ppm. The signals regarding glyceride backbone carbons were fully disappeared; whereas, a new signal corresponds to methoxy carbon was appeared at 51.4 ppm (Tahira et al., 2012). All abovementioned observations found in ¹³C NMR spectral analysis have confirmed that biodiesel was the transesterification product of WFO; moreover, it successfully justified the aspects stated for ¹H NMR analysis.

3.6. GC-MS analysis of waste frying oil biodiesel

The Gas chromatography-Mass Spectroscopy is powerful analytical technique to identify the organic composition of an analytical mixture. The constituent fatty acid methyl esters (FAMEs) of waste frying oil biodiesel were qualitatively and quantitatively analyzed by GC–MS. Such compositional analysis of these two feedstocks was performed on Agilent 6890 N gas chromatograph equipped with Agilent 5977 mass spectrometer. The gas chromatograph was outfitted with an Agilent Db-

225 capillary (30 m \times 25 mm \times 0.25 μ m). The column temperature was set to 160 °C for 2 min. Then it was increased to 230 °C at 5 °C/ min. Then it was held at 230 °C for 20 min. Nitrogen, was passed into the column with 1.0 ml/min flow rate. Inlet temperature was fixed at 250 °C, and the split ratio was maintained at 50:1. Flame ionization detector (FID) was used, and the detector temperature was kept up 280 °C. Supelco 37 Component FAME Mix (CRM 47885) was used as standard material. The obtained data were compared with NIST database for identification of fatty acid methyl esters in synthesized biodiesel samples. In Table S3 (see supporting information), the constituent fatty acids methyl esters present in synthesized biodiesel (WFOME, i.e. biodiesel produced from waste frying oil) are enlisted with their compositional percentage. The major five components were methyl α -linolenate (13.12%), methyl palmitate (4.92%), methyl oleate (30.20%), methyl linolinate (44.70%), methyl stearate (4.72%). The saturated FAME content in WFOME was found to be 19.13%; mono unsaturated FAME content and polyunsaturated FAME content were found to be 31.45% and 49.42% respectively. WFOME has good combusible property and high power output because of higher degree of unsaturation in FAME consituents (Ibadurrohman et al., 2021).

3.7. Physicochemical properties of product biodiesel

The product biodiesel will be considered as substituted diesel fuel when it successfully meets the standards of various important physicochemical properties mentioned by the American Society for Testing and Materials (ASTM). So, some of the most imperative properties of derived biodiesel have been evaluated by following ASTM standard methods and enlisted in Table S4 (see supporting information) with mentioning their permissible limit described in ASTM 6751. It is clearly shown in the above-mentioned table that the parameters of synthesized biodiesel such as the density at 40 °C (in g/l), kinematic viscosity (in mm²/s), acid value (in mg KOH/g), glycerin content (in wt %), calorific value (MJ/Kg), cetane number, cloud point (°C), flash point (°C), and pour point (°C) have obtained in acceptable range for biodiesel defined by ASTM standard. This has assured that the biodiesel derived from WFO is a compatible and potential biofuel for using in diesel engine (i.e. CI engine).

3.8. Comparative study of endurance capability of KSO 700 and KSO 800 catalysts

The key factor for choosing heterogeneous catalyst over homogeneous catalyst is reusability. A reusable catalyst may cut the production cost at larger extent. Thus, a catalyst which shows greater endurance with immense activity in terms of conversion or yield can be granted as efficient catalyst for economic biodiesel production. The endurance capability of KSO 700 and KSO 800 have been represented in terms of FAME conversion (%) in Fig. S8 (see supporting information). After completion of each run, the catalyst was removed by easy filtration process using Whattman40 filter paper and washed (three times) subsequently by using methanol and isopropanol. Then it was dried in air oven and recalcined at 600 °C for 2 h before using it in next run. KSO 800 showed more than 80% conversion up to 4th run and around 75 % after 5th run; whereas, KSO 700 showed significant endurance only up to 3rd catalytic run. Comparatively, in case of KSO 700, greater fall in FAME conversion has been observed in last two runs. This might be happened due to greater leaching of potassium species (KNO2 & K2CO3) present in KSO 700 (da Costa Evangelista et al., 2016). It is reported that the potassium species has high leaching tendency which was investigated in our study by hot filtration leaching test. In this method, 1 g of catalyst sample was separately stirred in 50 ml of methanol at 65 °C. After 1 hr, the solution mixture was filtrated and the methanol was collected to use in transesterification reaction conducted in optimized reaction condition but without using catalyst. KSO 700 showed around 7% FAME conversion but KSO 800 showed no FAME conversion in the hot filtration test. This means K-species present in KSO 700 were leached and came out to the methanol which acted as a catalyst in the further transesterification process. However, no leaching has been noticed in the case of KSO 800 but the slight decay (3% to 5%) in catalytic efficiency was recorded after each catalytic run, which was possibly occurred due to weight loss of catalyst in filtration process or deformation of the catalytic site in recalcination process or unwanted glycerol deposition at the active site (Sahani et al., 2019). So, considering endurance potency it can be confidently stated that KSO 800 is an efficient catalyst for economic biodiesel production.

3.9. Determination of 'Green factors' of the process

Under optimized reaction condition, the transesterification reaction of WFO using KSO catalysts is evaluated with respect to green parameters namely: yield, turnover frequency (TOF), environmental factor (Efactor), Atom Economy (AE), Process Mass Index (PMI), Mass Productivity (MP) and Reaction Mass Efficiency (RME). These factors will ultimately decide that the above process is green or not.

3.9.1. Yield of biodiesel

Yield of the product biodiesel can be defined as the following equation (Vicente et al., 2007):

$$Yield(\%) = \frac{weight of produced biodiesel(g)}{weight of WFO used(g)} \times 100$$
(13)

Yield of transesterification process using KSO 700 and KSO 800 catalysts were found to be 62% and 96% under the following reaction condition: 1 : 16 oil to methanol molar ratio, 3 wt% catalyst weight, 65 °C reaction temperature, and 35 min duration. Thus it is clearly noted that KSO 800 is much efficient than KSO 700 to produce biodiesel from WFO under moderated reaction condition.

3.9.2. Turnover frequency (TOF)

It is defined as number of moles of product has been produced at single basic site per unit time (Abdul et al., 2015). Number of basic sites present in catalyst can be determined from the basicity of the catalyst which is considered in millimoles per gram (Yadav and Sharma, 2019). Time corresponds the optimized reaction duration in second.

$$Turnover frquency = \frac{molesofbiodiesel}{basicity \times 10^{-3} \times time(s)}$$
(14)

In aforementioned transesterification reaction, the number of moles of biodiesel produced by using KSO 700 and KSO 800 catalyst were 0.057 and 0.088 respectively. The basicity of such catalysts was determined previously by Hammett indicator-titration method and it was found to be 1.21 mmol for KSO 700 and 1.76 mmol for KSO 800. Optimum time has taken as 35 min or 2100 s. Then using equation (14) TOF was calculated to be $22.3 \times 10^{-3} \text{ s}^{-1}$ for KSO 700 catalyst and $23.9 \times 10^{-3} \text{ s}^{-1}$ for KSO 800. These TOF results of the corresponding catalysts are high enough and almost comparable to the catalysts used in current industry level production (Sani et al., 2014).

3.9.3. Environmental-factor (E-factor), atom economy (AE), process mass index (PMI), mass productivity (MP) and reaction mass efficiency (RME)

The extent of cleanness is subjected to amount of waste generated during the process. The pathway produced lower amount of waste would be considered as cleaner or greener pathway. Thus, the cleanness or greenness of the transesterification process of WFO catalysed by KSO 700 and KSO 800 catalysts were get to know by calculating the green parameters namely E-factor, atom economy, process mass index, mass productivity and reaction mass efficiency using the following equations given below (Alagumalai et al., 2021; Yadav and Sharma, 2019, Gude and Martinez-Guerra, 2017).

$$E - factor = \frac{Producedwastemassing}{Producedbiodieselmassing}$$
(15)
AtomEconomy(AE)

$$= \frac{Molecularweight of biodiesel}{molecularweight of (oil + alcohol)}$$
(16)

ProcessMassIndex(PMI)

$$=\frac{Totalmassusedintransesterification process}{Produced biodieselmassing}$$
(17)

$$MassProductivity(MP) = \frac{1}{PMI} \times 100$$
(18)

ReactionMassEfficiency(RME) Massofthiodiasal + glycarol)

$$= \frac{Massof(biodiesel + glycerol)}{Massof(oil + alcohol)} \times 100$$
(19)

In transesterification reaction glycerol and unreacted triglyceride have been considered as waste product. Other substances like solvents and catalyst were excluded from the list of waste. Actually solvents like methanol and ethanol were distilled and reused in next cycle; similarly catalyst was also recovered and recycled for next batch runs. The produced waste mass in transesterification reaction catalysed by KSO 700 and KSO 800 were obtained 6.77 g and 1.96 g correspondingly. In these transesterification reactions 17.52 g of oil, 10.3 g of methanol and 0.52 g of catalyst were used with accurate measurement. The atom economy of the transesterification of WFO (irrespective of catalyst) was found to be 0.922. The value of E-factors of the corresponding transesterification reaction catalysed by KSO 700 and KSO 800 were calculated to be 0.385 and 0.072; PMI were accounted to be 1.613 and 1.042; mass productivity were estimated to be 62% and 96%; and RME were calculated to be 65.38% and 99.3%. Comparing the resultant green parameters of the transesterification processes catalysed by KSO 800 and KSO 700 catalyst, it can be stated that KSO 800 catalysed transesterification reaction approached more cleaner and greener pathway than that of KSO 700.

Moreover, activity in order to yield or conversion (%) of some of important catalysts reported in past few years for biodiesel production has been compared with KSO 800 in Table S5 (see supporting information). This comparative study has suggested that KSO 800 can be accepted as a potential catalyst for industry level production of biodiesel from waste frying oil.

4. Conclusion

This work has reported the liquid waste management of waste frying oil by converting in biodiesel, which encourages waste to fuel production. This was conducted via solid base catalysed transesterification process. Novel potassium - tin oxide catalyst was synthesized via polymer precursor - auto combustion method. Aftermath, the physical and chemical properties of the synthesized catalyst were investigated by various characterization techniques. TGA-DTA indicated that the potassium stannate phase of the catalyst was thermally stabilized at 791.7 °C and existed upto 846.3 °C. XRD reveled the different phases present in KSO catalyst calcined at different time, moreover, the phase evolution with time at constant calcination temperature. Carbonate free potassium stannate phase was achieved at 800 °C after 5 h calcination duration. XPS confirmed the oxidation states of K, Sn & O present in KSO 700 and KSO 800 catalysts. In SEM-EDAX the individual phases of potassium stannate compounds present in KSO 700 and KSO 800 catalysts were identified and cross-checked the results of XRD and XPS. BET surface area analysis and basicity suggested that increasing the catalyst calcination temperature improved the surface properties as well as basic strength. So, all due respect, it has been concluded that KSO 800 has better physicochemical properties than KSO 700. Thereafter, the catalysts were introduced in transesterification process. It was found that among other KSO catalysts, KSO 800 showed best activity when it was calcined for 5 h. Then KSO 800 was preceded for further optimizations of reaction parameters. This affirmed that the optimized reaction condition for KSO 800 catalysts transesterification of WFO was 1 : 16 oil to methanol molar ratio, 3 wt% catalyst weight, 65 °C reaction temperature and 35 min reaction duration. At this optimized reaction condition KSO 800 showed 99.5 % FAME conversion and 96% yield. Kinetic and thermodynamic study of this reaction disclosed that the reaction was a non-spontaneous exothermic reaction which followed pseudo-first order kinetic reaction pathway. Activation energy of this reaction was accounted to be 66.52 kJ/mol and thermodynamic parameters like $\Delta H^{\#}$, $\Delta S^{\#}$ and $\Delta G^{\#}$ (at 65 °C) were determined to be 62.95 kJ/mol, -74.07 J/mol/K and 88 kJ/mol respectively. Catalyst endurance study ensured that in case of KSO 800 leaching of K species was prevented, thus it showed activity above 75% after 5th catalytic run. At the end of this work, it was proved by 'green factor' study that KSO 800 catalysis followed greener and cleaner route with high efficiency comparable with homogeneous catalysts. So, it is finally concluded that KSO is an efficient, stable, reusable and leaching proof catalyst for faster and high quality biodiesel production; moreover, the environmental issues generated by WFO is smartly resolved by transforming it into biodiesel which can ultimately help in betterment of the nation's economy.

Uncited references

Badday et al. (2013), Fan et al. (2012), Gardy et al. (2019), Gude and Martinez-Guerra (2018), Hernández-Hipólito et al. (2015), Junior et al. (2019), Li et al. (2014), Liu et al. (2016), Mahesh et al. (2015), Saeedi et al. (2016), Sahani and Sharma (2018), Stambolova et al. (2005), Zhang et al. (2012).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.wasman.2021.08.046.

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