



Full Length Article

Characterization and upgradation of crude tire pyrolysis oil (CTPO) obtained from a rotating autoclave reactor

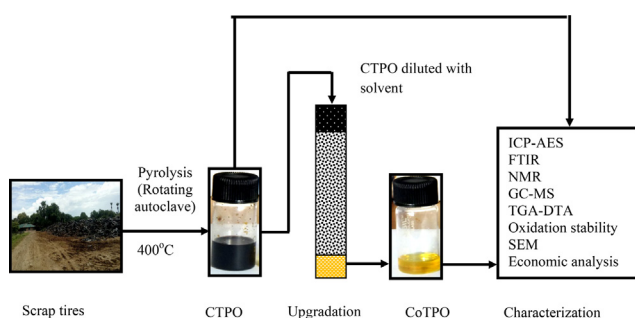
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GRAPHICAL ABSTRACT



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ABSTRACT

Many of the inferior fuel properties of crude tire pyrolysis oil (CTPO) can be attributed to the presence of polar organic compounds such as various oxygenates, nitrogen heterocycles and sulfur-containing compounds. An efficient, straightforward and scalable pathway of removing the polar fraction from CTPO is crucial in improving its fuel properties. In this work, CTPO produced by thermal pyrolysis (400 °C, 0.2 bar, 4 rpm, 5 h) of scrap automotive tires in a rotating autoclave reactor (8-tons) has been upgraded using silica gel (60–120 mesh) as adsorbent and petroleum ether as diluent. In two different strategies, CTPO was first diluted with petroleum ether and (1) passed through a column of silica gel (CoTPO) or (2) mechanically stirred with silica gel (StTPO) followed by solvent evaporation to afford upgraded oil. Both crude and upgraded TPO samples were extensively analyzed for chemical composition and fuel properties and compared with each other. Analytical techniques like GC-MS, ¹H NMR, FTIR, and elemental analysis showed significantly less polar fractions in CoTPO and StTPO compared to CTPO. The cetane index of CoTPO and StTPO were found to be 35 and 40, respectively compared to 33 in CTPO. Sulfur content decreased by 19% and 34% in CoTPO and StTPO, respectively. The acid value of CoTPO and StTPO were found to be 0.8 and 0.6 compared to 12.2 in CTPO. The TGA data showed better thermal stability of upgraded oil samples. StTPO showed better chemical composition and fuel properties compared to CoTPO that can be explained by its longer contact time with silica gel adsorbent.

1. Introduction

With increasing production of automotive tires, the problem of

accumulating end-of-life scrap tires adds to be already existing problem of waste tire management. It was estimated that 1.5 billion tons of waste tires are being generated every year [1,2]. These scrap tires are

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mostly dumped into the land-fills. The non-biodegradable and voluminous nature of tires make storage expensive. Improper disposal of scrap tire waste leads to nuisance like blockage of water drainage systems and also poses serious public health hazards [3,4]. Uncontrolled combustion of scrap tire generates toxic organic and inorganic pollutants and create environmental and health hazards [5].

There has been a coordinated attempt over the past several years in developing novel technologies for generating useful liquid, gaseous and solid products from tire waste. Pyrolysis is a thermochemical conversion method for depolymerizing the polymers in scrap tires in an oxygen free environment. The rubber (natural and synthetic) polymers are broken down into small organic molecules (liquid and gas) and also solid char. The volatile gaseous products are generally burned to generate process heat. The liquid product, also known as crude tire pyrolysis oil (CTPO), can be used as an alternative engine and furnace fuel [6]. CTPO is a complex mixture of C_6 - C_{24} organic compounds such as paraffins, olefins, terpenes, mono and poly aromatics, nitrogen and sulfur containing heterocycles and oxygenates [7,8]. The major obstacles of CTPO for direct use as engine and furnace fuel include unpleasant odor, high acidity, poor combustion properties, high sulfur content, poor storage stability and low thermal stability. Therefore, inexpensive, effective, and scalable upgrading of CTPO has garnered serious attention from both the academic and industrial community around the world. Upgrading strategy of CTPO reported in the literature include hydro-refining, adsorption over activated carbon [6], hydro-processing [8], hydro-treating [9], catalytic upgrading [10–12], copyrolysis [13], and fractional distillation [14]. Hydro-refining of CTPO was conducted in the presence of commercial catalyst like CoMo-SiO₂-Al₂O₃ and NiMo-Al₂O₃ in a hydro-refining apparatus at 360 °C and hydrogen pressure of 5 MPa [1]. The CoMo-SiO₂-Al₂O₃ catalyst was able to reduce the sulfur content from 1.1% to 0.2% and NiMo-Al₂O₃ decreased the sulfur content to only 0.1%. Hydro-treating of CTPO was carried out using various catalysts such as γ -Al₂O₃ (ALM), SiO₂-Al₂O₃, SBA-15, and MCM-41 and equilibrated FCC catalyst in a fixed bed reactor at 275–375 °C and 65 bar hydrogen. The results showed that usage of ALM catalyst significantly improves the cetane number by 5 units and 90% sulfur reduction in CTPO [9]. Han et al. studied the co-pyrolysis of tire pyrolysis oil and vegetable oil in a 250 mL Parr reactor with a stirring speed of 250 rpm. The hydrogen was supplied at a pressure of 9.1 MPa at room temperature during the reaction. They found that the refined oil had higher H/C ratio, flash point and kinematic viscosity in comparison with conventional petroleum-derived fuels [11]. CTPO was upgraded within a temperature of 300–400 °C at an initial hydrogen pressure of 4 and 7 MPa in absence and presence of bimetallic (e.g., Co-Ni, Co-Mo and Ni-Mo) catalysts. The TPO [tire pyrolysis oil] was found to be suitable as a transportation fuel [12]. Copyrolysis of forestry biomass and waste tires was carried out in a fixed bed reactor (500 °C, 80 °C/min, 15 min) and continuously auger reactor (500 °C, flowing N₂, mass flow 5 kg/h) [13]. The results showed that addition of waste tire significantly reduced the amount of oxygenates in bio-oil and improved its stability. Impact of copper on various type of zeolites (HBETA, HY and HMOR) in a bench reactor (500 °C, 10 °C/min, 90 min). Cu-promoted catalyst was found to be more effective in reducing the sulfur content in CTPO [14]. Obadiah et al. [15] characterized the distilled TPO for its potential as a supplementary fuel in diesel engines. The fractional distillation was carried out in a 500 mL round-bottomed flask attached to a column packed with steel wool. Although viscosity, density and corrosiveness of the distilled fuel were found to be within acceptable limits, the sulfur content and flash point of the fuel were higher than desired. Hita et al. [16] studied the performance of activated carbon-supported Ni-Mo bimetallic catalysts on crude TPO in a fixed-bed reactor (275–375 °C, 65 bar H₂, space time 0.16 h). Hydro-processing of tire oil with Ni-Mo catalyst reduced 96.3% of sulfur. Undri et al. conducted tire pyrolysis experiments in a batch-type oven (2.45 GHz, 6 kW) connected to a fractionating system. The experiments resulted in a pale-yellow transparent liquid, rich in

aromatics and olefins.[17]. Ucar et al. co-pyrolysed pine nut shells and scrap tires at 500 °C under an inert atmosphere of nitrogen in a stainless-steel reactor [18]. They reported that addition of pine-nut to scrap tires improved the yield and physicochemical properties of the resultant fuel oil. As evident in the literature, most of the inferior properties in CTPO can be attributed to the sulfur, nitrogen, and oxygen-containing polar compounds present in it. Therefore, selective removal of the polar components from CTPO will lead to fuel oil with better properties.

In present study, a mixture of end-of-life automotive tires has been thermally pyrolyzed in a rotating autoclave reactor and the resultant crude TPO extensively characterized for chemical composition and fuel properties using analytical techniques such as Fourier transform infrared spectroscopy (FT-IR), gas chromatography-mass spectrometry (GC-MS), thermo-gravimetric analysis (TGA), thermal stability, inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The present study presents a novel, efficient, and scalable upgrading of CTPO using a combination of selective adsorbent and non-polar diluent. CTPO diluted with petroleum ether was either passed through a fixed-bed column of silica gel adsorbent (CoTPO) or mechanically stirring with silica gel (StTPO). The upgraded TPO oil samples obtained after removing the diluent were characterized for chemical composition and their fuel properties were compared with CTPO.

2. Experimental methodology

2.1. Materials

CTPO was obtained by the thermal pyrolysis of scrap automotive tires in a rotating autoclave reactor at Mandakan Energy Products, Kerala, India. Silica gel (60–120 mesh) and petroleum ether (60–80 °C) were purchased from Sigma Aldrich [27].

2.2. Pyrolysis procedure

Pyrolysis is a thermochemical destruction of solid waste like tire and plastics in an oxygen free atmosphere. The major factors which affect the pyrolysis operation are pressure, temperature, feed size, retention time, configuration of reactor and so on. Several researchers have used various types of reactor used for thermochemical conversion of solid wastes like fixed bed, auger, rotary, fluidized bed, continuous, vortex, externally retort type, plasma, vacuum, microwave, radiofrequency [2]. Fixed bed reactors are widely used for the pyrolysis of scrap tires. The pyrolysis of 10 g tire is carried out in a nitrogen purged fixed bed reactor at a heating rate of 10 °C/min. The maximum oil yield (60 wt%) was obtained at 425 °C [19]. Aylon et al. [20] used moving screw bed reactor for tire pyrolysis between 600 and 800 °C. Compared with rotating autoclave, the moving screw bed reactor was fed by a screw feeder from the hopper. The maximum yield of 48.4 wt% was obtained at a pyrolysis temperature of 600 °C and 8 kg h⁻¹. Williams and Brindle [21] used fluidized bed reactor for the pyrolysis of 220 kg h⁻¹ throughput and a temperature range of 450–600 °C reported that there was an increase in the hydrogen and hydrocarbon composition by increase in temperature. Olazar et al. [22] used conical spouted bed reactor. The spouted bed is a type of fluidized bed reactor, which enhances the heat transfer rate, reduction in gas residence time (minimizes the secondary reactions). Vacuum pyrolysis of waste tires was investigated by Zhang et al. and co-workers [23] using batch-type vacuum pyrolysis reactor for the pyrolysis of tire granules and reported that the yield of the pyrolysis oil drastically increased, when the temperature was raised from 450 to 600 °C. A drop tube pyrolysis reactor was used for the pyrolysis of waste tire particles (4 mm) by Conesa et al. [24]. The increase in pyrolysis temperature showed a marked reduction of oil yield from 37.8 wt% to less than 0.001 wt% at 1000 °C. Galvagno et al. [25] reported that the operation of rotating autoclave between 550 and 680 °C improved the gaseous composition (hydrogen, carbon monoxide, methane, ethane, ethene and higher hydrocarbons).

Table 1
Comparison of rotating autoclave reactor with other reactors used in the pyrolysis of scrap tires.

Type of reactor	Tire feed	Reaction conditions	Yield of TPO [#] (wt%)	References
Fixed bed	10 g	375–500 °C, 10 °C min ⁻¹	60	[19]
Moving screw bed	–	600–800 °C, 10 °C min ⁻¹	48	[20]
Fluidized bed	220 g/h	450–600 °C, 10 °C min ⁻¹	55	[21]
Conical spouted bed	–	425 and 500 °C	62	[22]
Vacuum pyrolysis batch reactor	100 g	450–600 °C	47	[23]
Drop tube reactor	30 g/h	450–1000 °C	38	[24]
Rotating autoclave	4.8 kg/h	550–680 °C	38	[25]
Rotating autoclave*	8-ton	400 °C, 10 °C min ⁻¹	44	Present study

[#] Product yield is average of two experiments.

* Study carried out at Mandakan Energy Products, Kerala, India.

However, the proposed study used 8 tons of whole tire waste (mixture of tires) in a rotating autoclave operating in the range of 400–430 °C at a heating rate of 10 °C/min and obtained a maximum yield of 3.5 tons. Table 1 reports the common types of reactors used for TPO production and a comparative study with the present study using rotating autoclave reactor.

A mixture of end-of-life automotive tires was used as feed for thermal pyrolysis. The experiments were carried out at a temperature of 400 °C (heating rate 10 °C/min) in a rotating autoclave reactor with a capacity of eight tons. The optimized residence time was 5 h for best yield of TPO. Since the tires were sliced and fed directly into the reactor without further reduction in size, relatively longer residence time was required for pyrolysis. The residence time can be shortened significantly by using smaller and uniform particle size of the tire feed. The schematic illustration of the pyrolysis plant is given in Fig. 2. The system has several components like reactor, primary pressure reactor, electronic control panel, non-condensable gas tank, scrubber with blowers and pumps, condenser, water spray tower and gas storing balloons. The cylindrical shape reactor is the main part of the system. The reactor is 6.6 m in length, 2.8 m in diameter and has a capacity of 10 ton. The reactor is rotated externally with the help of motor attached with gear and pulley arrangement. Initially, the reactor was heated by

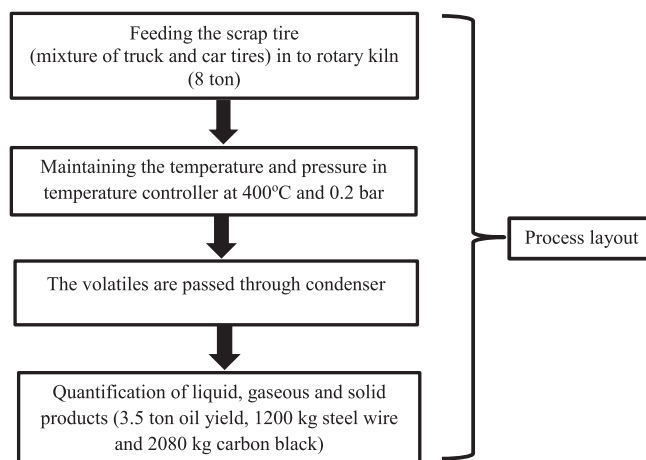


Fig. 2. Process layout of the 10 tone pilot scale rotating autoclave.

burning wood but in the later stage of pyrolysis experiments, the non-condensable gases stored in the gas storage system was used as fuel for three furnaces attached at the bottom of rotating autoclave reactor. A

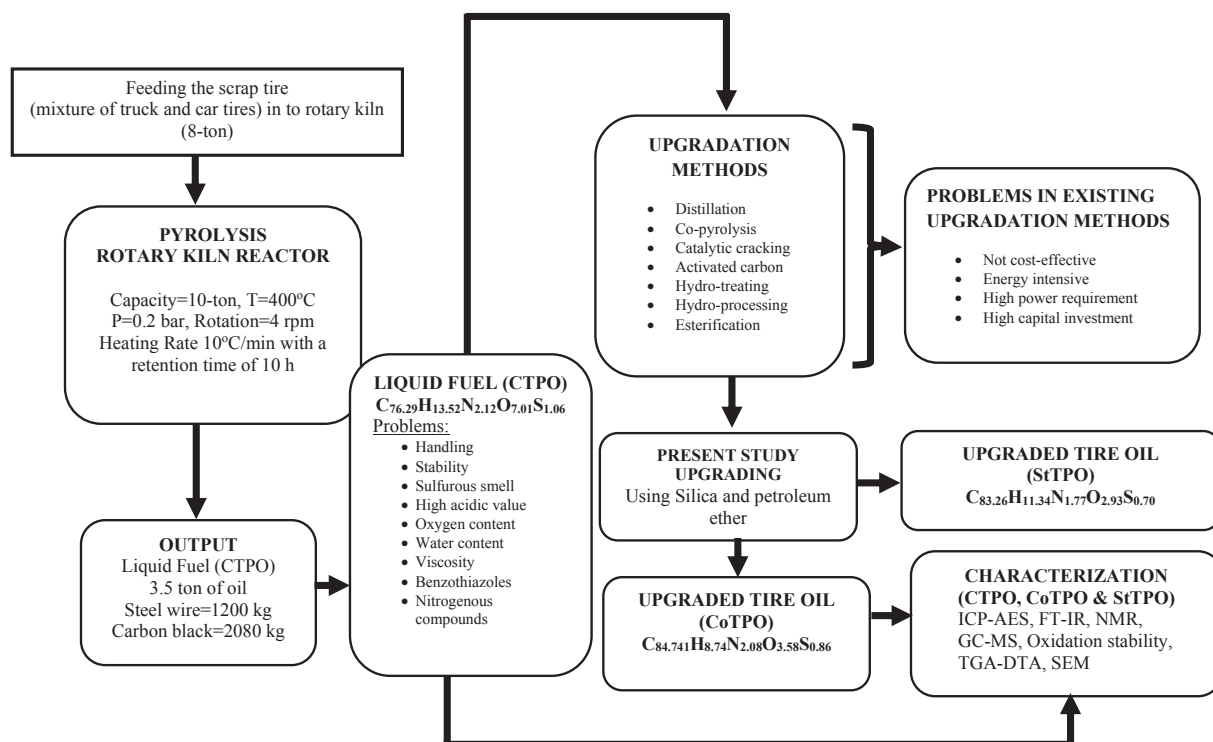


Fig. 1. Schematic of methodologies used in the present study.

mixture of car tire and truck tire were fed in the reactor through the front door, which can be opened or closed with the help of fasteners. The other end of the reactor is connected to a condenser through a flexible connection and a sealing element. The volatiles formed during pyrolysis was passed through the condenser pipes in a water-cooled chamber. The liquid condensate was stored in storage tanks and the non-condensable gases were stored in gas-storing balloons. The cooling tower helped to maintain the temperature of coolant to atmospheric temperature. A control panel controls the whole setup and accessories. The pyrolysis of 8-ton of tire yields 3.5 ton of TPO, 1200 kg of steel wire and 2080 kg of carbon-rich char. Fig. 1. shows the pyrolysis parameters in the industry, product distribution, problems of CTPO, existing upgradation methods, novel upgradation strategy, problems of existing upgradation strategy and characterization technique involvement in the present study. The process layout of production process is shown in Fig. 2.

2.3. Procedure for upgrading CTPO

2.3.1. Upgradation of CTPO using glass column packed with silica gel

Preferential solubility and selective adsorption were used in the present study to upgrade CTPO obtained from pilot scale rotating autoclave reactor. A glass column of diameter 2.5 cm, column bed height of 50 cm was used for the present study. The column was filled with a bed of 150 g silica gel (60–120 mesh). 450 mL of petroleum ether was mixed with 150 mL of CTPO and obtained slurry was passed through the bed of silica. Additional 50 mL of petroleum ether was used to elute CTPO from the column of silica gel. The different compounds in CTPO have different interaction with the mobile phase (petroleum ether) and stationary phase (silica gel) in the glass column. The obtained fraction was collected in an Erlenmeyer flask and named as CoTPO. Petroleum ether was recovered using rotary evaporator under 3-in. Hg to get refined CTPO (26 mL). The polar fraction in the crude pyrolysis oil was adsorbed selectively by using silica column and the obtained oil was found to be better in terms of both appearance and chemical composition. The used silica gel can be recovered by washing with a polar solvent like methanol or through calcination processes. The obtained CoTPO (golden yellowish) was better in terms of appearance and stability. Fig. 3. shows the selective adsorption of CTPO using silica column strategy.

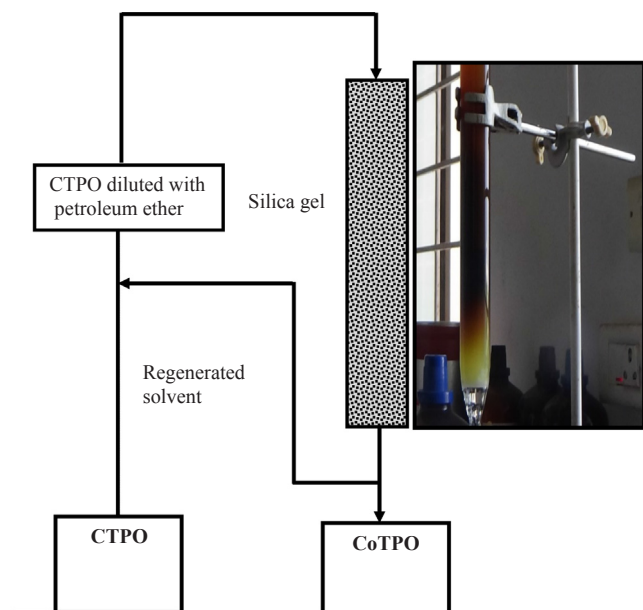


Fig. 3. Upgrading of crude TPO using column strategy.



Fig. 4. Upgrading of CTPO by mechanically stirring a suspension of silica gel in diluted CTPO.

2.3.2. Upgradation of CTPO using magnetic stirrer

CTPO (100 mL) was stirred using a magnetic stirrer and then petroleum ether of 300 mL was added to it. Then the solution was stirred at room temperature for 15 min. The supernatant was decanted into another 500 mL conical flask containing 100 g silica gel (60–120 mesh). The suspension was stirred magnetically for 1 h. Then, the solution was filtered under vacuum and the silica gel was washed with fresh petroleum ether (100 mL). The petroleum ether fractions were combined and evaporated in a rotary evaporator at 60 °C under reduced pressure (3 in. Hg). The yield of reddish brown colored upgraded oil (CTPO) was 85 mL. Fig. 4 shows the stirring strategy used for upgradation of CTPO.

2.4. Characterization of CTPO, CoTPO and StTPO

The elemental composition of CTPO, CoTPO and StTPO were determined using an elemental analyzer (CHNS-O Flash EA 1112 Series) to find out the percentage of carbon, hydrogen, nitrogen and sulfur. The oxygen content was calculated by difference. Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) is widely used for the detection of metallic elements present in the oil using microwave assisted acid digestion. The present study used ICP-AES for qualitative and quantitative estimation of various metallic elements present in CTPO using ARCOS, simultaneous ICP spectrometer. The identification of organic functional groups in the pyrolytic oil were carried out by using FTIR (3000 Hyperion Microscope with Vertex 80 FTIR System) with data processing and library search facilities. The IR spectra of the oil samples were collected in the spectral range between 4000–400 cm^{-1} . The $^1\text{H-NMR}$ spectrum of the pyrolytic oil was recorded in a Bruker Advance III 500 MHz instrument using deuterated acetone as the NMR solvent. GC-HRMS analysis of TPO was carried out to find the chemical composition of oil with the help of an Accu-TOF GCV7890, Joel GC-HRMS analyzer (DB-petro column, cross linked 5% methyl phenyl silicone, 50 m * 0.25 mm ID, 0.5 μm film thickness) was used. Helium of purity 99.99% was used as a carrier gas at a constant rate of 1 mL min^{-1} . GC oven temperature was programmed from 50 °C to 270 °C at a ramping rate of 10 °C/min and held for 2 min. The total runtime was 45 min. The mass spectra of the compounds were identified from the respective GC chromatograms using National Institute of Standards and Technology (NIST) library. The thermal behavior of the pyrolytic oils were studied using TG/DTA. About 9.73 mg of the sample was placed in an alumina crucible covered with a perforated lid and heated from 30 to 300 °C at a rate of 10 °C/min. Thermal decomposition behavior of TPO samples were carried out using NETZSCH DSC 204 under a heating rate of 10 °C/min. The gas flow rate was kept constant at 50 mL/min during the experiments. The oxidation stability gives an idea about how the CTPO and upgraded TPO behaves with rise in the temperature. In a typical experiment, 5 mL of TPO was taken in a 10 mL beaker and kept for 24 h at 120 °C in a convection oven for the oxidation stability analysis of CoTPO and CTPO. Fig. 5. shows the

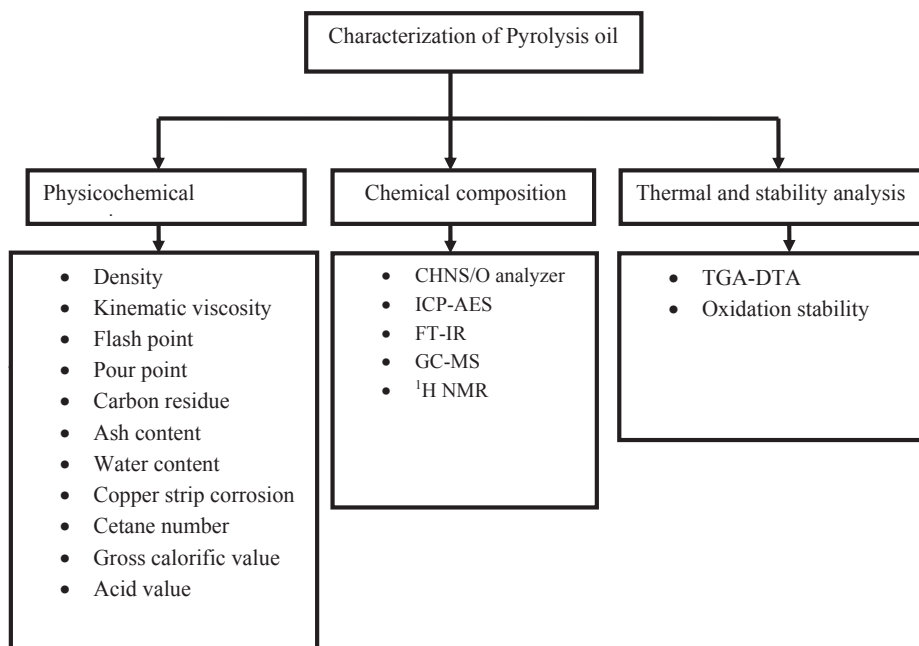


Fig. 5. Characterization and analysis used in the present study.

characterization and analysis techniques proposed in the present study.

3. Results and discussion

3.1. Effect of upgrading on the physicochemical and thermal properties of upgraded TPO samples

Automobile tires are made of natural and synthetic rubbers that all have hydrocarbon backbone and/or side chains. Scission of carbon–carbon bonds in the polymer chains into smaller fragments (ca. C₁₂–C₂₂) could lead to diesel-like hydrocarbons. However, automobile tire also contains polar compounds like inorganic solids, sulfur compounds, anti-oxidants, and other polar organic additives. Polar compounds also get generated by air-oxidation of tire polymers during its lifetime and storage. The CTPO used in this study contain nitrogen, sulfur and oxygen-containing compounds as evident in the GC chromatogram, ¹H NMR spectrum, and FTIR spectrum. Many of the inferior fuel properties of CTPO including poor storage and thermal stability, lower heating value, low cetane index, high sulfur content, and high acid value are due to the polar compounds present in it. A selective, scalable and economic strategy in removing polar fractions from TPO is important for the economic viability in using TPO as a diesel substitute. Fractional distillation is a commonly used strategy in separating various fractions while discarding higher boiling polar fractions. However, the process is energy intensive, require relatively expensive equipment and generally low-yielding. We argued that the polar fractions in CTPO can be preferentially removed under milder conditions by using an adsorbent. Silica gel is a commonly used adsorbent in organic chemistry laboratories for separating a mixture of compounds based on their polarity index. The non-polar hydrocarbons have minimum interaction with silica gel whereas the polar compounds preferentially adsorb on silica gel. An inert, inexpensive, non-polar, and easily recoverable solvent or diluent is required so that the physical hold up of CTPO on silica gel is minimized. Petroleum ether was chosen as a solvent for this purpose. The CTPO was diluted with petroleum ether and any insoluble residue was discarded. The diluted CTPO was passed through a column of silica gel (CoTPO) or stirred mechanically with silica gel (StTPO). After the stipulated time, the suspension was filtered and the solvent was evaporated under reduced pressure to get upgraded TPO. The used silica gel was regenerated by calcining in air at 800 °C and petroleum

ether was recycled by distillation. The chemical composition and fuel properties of both CoTPO and StTPO were analyzed and compared against CTPO. As expected, both CoTPO and StTPO have significantly less polar compounds as indicated by the GC–MS and ¹H NMR analyses and also the elemental analysis. The fuel properties of CoTPO and StTPO improved significantly over CTPO and are comparable to petrodiesel (Table 5). For example, the acid value in CoTPO and StTPO decreased by more than an order of magnitude compared to CTPO which can be explained by the removal of acidic oxygenates like carboxylic acid. The storage and thermal stability improved significantly as confirmed by TGA data. This improvement can be explained by removal of unstable polar compounds like aldehydes and carboxylic acids that catalyze polymerization of olefins present in CTPO. The percentage of nitrogen, oxygen and sulfur in CoTPO and StTPO decreased considerably and the H/C molar ratio matches closely with diesel fuel. StTPO shows better fuel properties than CoTPO since its contact time with silica gel was longer helping more efficient removal of polar fractions.

3.2. Elemental analysis and chemical composition

Pyrolytic oil from polymer materials contains host of metallic elements and is very difficult to quantify them. The crude and upgraded pyrolytic oil were digested according to EPA method 3051A (microwave assisted digestion of oils) and then analyzed according to EPA method 200.7 using ICP-AES. The result shows that the CTPO contains boron, calcium, iron, magnesium, manganese, sodium, sulfur, silicon, strontium, titanium and zinc whereas the CoTPO contains boron, calcium, iron, magnesium, sodium, sulfur, silicon, strontium, titanium, zinc, and zirconium. The composition of carbon and hydrogen in CTPO shows almost similar values in Ref. [20]. However, the nitrogen composition is much higher in TPO obtained from the rotating autoclave reactor due to presence of Nitrogen-containing compounds in feed tires (e.g., accelerator) which is significantly less in Ref. [20]. The nitrogen content in StTPO (1.77%) is significantly less compared with CoTPO (2.08%) and CTPO (2.12%) due to the higher contact time between TPO and silica gel in the stirring strategy. During the ICP-AES analysis, sulfur content in the CTPO, CoTPO and StTPO were found to be 1.06%, 0.86% and 0.7%, respectively.

The H/C ratio is higher for the CTPO in comparison with CTPO and

Table 2
ICP-AES analysis of CTPO, CoTPO and StTPO with diesel.

Element (wt%)	CTPO	CoTPO	StTPO	Raw Diesel [26]
Carbon (C)	76.29	84.74	83.26	87.4
Hydrogen (H)	13.52	8.74	11.34	12.1
Nitrogen (N)	2.12	2.08	1.77	0.039
Sulfur (S)	1.06	0.86	0.70	1.39
Oxygen (O) [*]	7.01	3.58	2.93	–
Vanadium	BDL	BDL	BDL	BDL
Zinc	BDL	BDL	BDL	BDL
Phosphorous	BDL	BDL	BDL	BDL
H/C [#]	2.11	1.23	1.62	1.65

* Calculated by difference.

Molar ratio.

diesel. However, the carbon content in CTPO (76.29%) is slightly lower than CoTPO (84.74%) and StTPO (83.26%) This indicated the huge number of carbon atom in the structure CoTPO attributes to high calorific value than CTPO. Table 2. shows the elemental composition of carbon, oxygen, vanadium, zinc, phosphorous and H/C ratio of CTPO, CoTPO, StTPO and a comparative study with diesel. The oxygenates in the upgraded oil obtained from stirring strategy is very low (2.93%) compared to CTPO due to adsorption of all polar compounds and oxygenates during the upgradation process.

3.3. Comparative study on fuel properties of CTPO, CoTPO and StTPO with diesel

This section describes the physicochemical properties of tire derived oil before and after upgradation and also compared with the properties of tire derived oil reported in the literature. Pyrolysis oil obtained from the scrap tire has strong pungent odor due to the huge number of organic compounds and looks like black in color. However, the oil obtained after the upgradation process has hydrocarbon-like odor and the color of the oil changed from black to light yellowish colored liquid due to adsorption of colored pigments by silica gel. Sulfur analysis plays an inevitable role in the pungent odor due to presence of Sulfur containing compounds in CTPO. The CTPO in the present study has 1.06% due to presence of sulfur-containing compounds such as mercaptan, benzothiazole, and dibenzothiophenes. The CoTPO and StTPO had 18.86% and 51.42% reduction of sulfur content, respectively. But, the elemental Sulfur content of CTPO, CoTPO and StTPO are slightly higher than diesel fuel [28] and the Sulfur content in CoTPO and StTPO is very lower in comparison with petroleum fuels [28]. The acidic value of CTPO, CoTPO and StTPO are 11.54, 0.8 and 0.6 respectively. The drastic reduction in the acidic value is due to adsorption of polar compounds in CTPO adsorbed by silica gel, which are identified using NMR and GC-MS spectra of CTPO, CoTPO and StTPO. Table 3 summarizes the comparison of CTPO and upgraded oil with industrial standards. Fig. SI 1–7 summarizes the detailed comparative study of physico-chemical properties of CTPO, CoTPO and StTPO with industrial standards are shown in Supplementary information (SI).

Ash content denotes the soluble organo-metallic compounds in an oil fraction. The StTPO in the present study has similar value of ash content (0.01%) in comparable with diesel standard, but the ash content in the CTPO and CoTPO are slightly higher (0.02%). The direct usage of 100% CTPO may cause severe deterioration in the fuel injection system by excessive deposition of suspended solids and organo-metallic compounds and hinders the smooth operation of diesel engine. However, StTPO can be directly be used in the diesel engine due its low ash content. The Calorific value of CTPO (41761 kJ/kg) measured by bomb calorimeter in the present study is similar to those reported in the literature [29–36]. However, the CTPO after upgradation (CoTPO and StTPO) showed an increase in calorific value by 540 kJ/kg and 1219 kJ/kg respectively. The rise in the calorific value in the upgraded

oils is due to the removal of low-energy polar compounds. More efficient removal of polar compounds results in higher calorific value in StTPO compared to CTPO and CoTPO. However, the calorific value of StTPO is slightly lower than the standard diesel fuel [35]. Carbon residue is a parameter which indicate the tendency of fuel to form carbonaceous deposits in the engine. Cetane index is a way to denote the quality of a fuel in diesel engines [36]. Cetane index is an approximation of cetane number based on the empirical relationship with density and volatility [35]. The CTPO, CoTPO and StTPO in the present study showed the cetane index as 33, 35 and 40 respectively. Thus, the StTPO showed a same value of cetane index when compared with diesel standards [35]. The present study shows that the density of CTPO, CoTPO and StTPO are higher than diesel fuels. Regarding the specification standards, the density of diesel and petroleum fuels are in the range of 0.799 and 0.78 respectively. The density of CTPO in the present study is very similar to other tire derived oil in the literatures [29–36]. The high density of CTPO in the present study means that the amount of fuel injected in to the engine per unit volume will be increased. Flash point represents the lowest temperature at which petroleum vapors will ignite under a lower flame. The flash point of CTPO, CoTPO and StTPO in the present study showed the flash point values of 52 °C, 46 °C and 32 °C. Flash point may vary due to the storage condition, condensation reaction during the long-term storage. The viscosity of StTPO is lowered than the viscosity of petroleum fuels. Literature has reported a wide range of viscosity values of tire derived oils [29–36]. The main reason for the reduction in the viscosity after upgradation is due to the adsorption of higher molecular weight compounds by silica gel. Upgraded TPO has viscosity close to diesel [30,33] and petroleum fuels [29].

3.4. FT-IR analysis

The C–H stretching vibrations (symmetric and antisymmetric in $-\text{CH}_2$ and $-\text{CH}_3$) appeared at 2951–2855 cm^{-1} and C–H bending vibrations between 966.12 and 698.86 cm^{-1} indicates the presence of alkanes. The C–H bending vibrations between 1454 and 1375 cm^{-1} indicates the presence of alkanes. Absorbance between 1650 and 1750 cm^{-1} represent the presence of carbonyl functionality such as ketone or aldehydes. Absorbance of C–H stretch above 3000 cm^{-1} shows the presence of aromatic hydrocarbons and or alkenes. Less intense peak in between 1600 and 1700 cm^{-1} indicates lower amount of oxygenated compounds in the CoTPO. The StTPO contains mostly aliphatic, aromatic and aromatic hydrocarbons and FT-IR spectrum appears much more straightforward. Fig. 6 illustrates the FT-IR spectra of CTPO and upgraded oils.

3.5. NMR spectroscopy

NMR studies are carried out using Bruker Advance III 500 MHz spectrometer and samples were dissolved in deuterated Methanol. Fig. SI 8(a), (b) and (c) showed the ^1H NMR spectrum and hydrogen distributions of crude tire pyrolytic oil obtained from rotating autoclave pyrolysis and upgraded pyrolytic oil, CoTPO and StTPO respectively. NMR spectra of CoTPO and StTPO showed that some troublesome compounds had been removed during refining. For example, the peaks above 8 ppm (parts per million), which are responsible for hetero aromatics like pyridine, benzothiophene, benzothiazole are removed. The oxygenates around 3.5–4.5 ppm are at a minimum in CoTPO and StTPO. The aldehyde peak at 9.6 ppm is no longer there in the NMR spectra of CoTPO and StTPO. Removal of aldehyde and carboxylic acids means that the acid value and oxidative stability of refined TPO will improve significantly. The presence of limonene in refined oil at 4.7 ppm and 5.4 ppm. NMR study revealed that the aliphatic compounds are pre-dominant than aromatics, oxygenates, aldehydes and ketones in CTPO (71.1%), CoTPO (86.98%) and StTPO (89.71). Same results were reported by Islam et al. [48]. Table 6 shows that various

Table 3
Comparative study on fuel property of CTPO, CoTPO and StTPO with industrial standards [31–32].

Properties	ASTM D975	ARAI [#]	MRPL [*] (BS IV)	MRPL [*] (BS III)	MRPL [*] (BS II)	CTPO	CoTPO	StTPO
Density (g/mL)	0.7994	–	0.80–0.845	0.80–0.845	0.80–0.860	0.907	0.8926	0.8682
Kinematic viscosity (cSt)	1.9	2.5–4	2–4.5	2–4.5	2 to 5	3.83	3.74	2.54
Flash point (°C)	52	32 min	35 min	35	35 min	52	46	32
Carbon (%)	–	–	–	–	–	76.29	84.74	83.259
Hydrogen (%)	–	–	–	–	–	13.52	8.74	11.343
Nitrogen (%)	–	–	–	–	–	2.12	2.081	1.766
Oxygen (%)	–	–	–	0.6	–	7.01	3.58	2.93
Sulfur as S (%)	0.05	–	–	–	–	1.06	0.86	0.7
Carbon residue (%)	0.35	–	0.30 max	0.3	0.30 max	0.2	0.21	0.2
Ash content (%)	0.01	0.20 max	0.01 max	–	0.01 max	0.02	0.02	0.01
Cetane index	40	45 min	Min 46	46	Min 46	33	35	40
Gross calorific value (kJ/kg)	45,814	–	–	–	45,814	41,761	42,221	42,980
Acid value (KOH/g)	–	0.5	Not worse than No.1	0.05	–	12.21	0.8	0.6
Copper corrosion (3 h at 50 °C)	–	1 max	–	–	Not worse than No.1	Not worse than No.1	Not worse than No.1	Not worse than No.1
Pour point (°C)	–	–	Max 6 (winter)	Max 6 (winter)	Max 6 (winter)	< –15	< –15	< –15

[#] ARAI – Automobile research association of India.

^{*} MRPL – Mangalore refinery and petrochemicals limited.

class of compounds and corresponding percentage of total hydrogen distribution in CTPO, CoTPO and StTPO. Table 4 illustrates the percentage of hydrogen in CTPO and upgraded oils.

3.6. GC–MS analysis

GC–MS analysis of CTPO and CoTPO were carried out to identify the compounds present in respective samples. The chromatogram of CTPO, CoTPO and StTPO is shown in Fig. 8. The compounds were identified with the help of NIST-08 library and were compared with the data reported in the literature [9,38,39]. The identified compounds and relative peak area percentage are presented in Tables 5–7. These compounds are grouped as aliphatic, aromatics, poly-aromatic hydrocarbons, and other compounds. These compounds are classified on related chemical structure properties and molecular weight by work of Ayanoglu et al. [37,40]. The analysis show that compound present in CTPO were similar to the results found in literature [38–41]. GC–MS analysis of CoTPO using present upgradation strategy using silica and petroleum ether were not found in the open literature. GC–MS analysis of CTPO is reported in Refs. [9,42–47]. GC–MS analysis supported with FT-IR analysis of CTPO revealed that the composition of aliphatic (47.69%), aromatics (2.99%) and other compounds (7.60%). The results were plotted for comparison in the Fig. 7 along with the present study. In CTPO, the composition of aliphatic and aromatics were found to be similar to those reported in the literature. In CoTPO, the aliphatic and aromatic compounds are found to be 24.65% and 11.92% whereas StTPO contains 53.25% and 23.341% respectively. The present study showed that drastic rise in the composition of aliphatic (5.56%) and aromatic composition (20.35) after stirring based upgradation strategy whereas there is a reduction in the aliphatic (23%) and increase in the aromatic compounds (8.93%) in case of CoTPO. The increase in aliphatic and aromatics in the stirring strategy is due to higher contact area of pyrolysis oil and silica surface facilitates the perfect adsorption. The main reason of reduction in PAH composition in CoTPO and StTPO is that silica retained in the column and magnetic stirrer adsorbs most of the polyaromatics due to large pore diameter (40–60 Å) and large surface area (350–450 m²/gm). The major limitation of GC–MS analysis is the difficulty to develop the calibration curve to predict the exact concentration of compounds in the CTPO, CoTPO and StTPO looks a very tedious task due to the overcrowding of wide range of compounds and can be practicable by using column chromatography will be planned in the future course of the study.

3.7. Thermogravimetric analysis (TGA)

TGA analysis shows the decomposition behavior of crude and upgraded tire pyrolytic oils. The results show that mainly three stages like drying and two decomposition zones. The initial stages of decomposition of CTPO starts at 30–75 °C but the variation is steeper in the case of CoTPO. The early decomposition is mainly due to the loss of moisture, loss of oils etc. This is followed by thermal decomposition at 250 °C. Williams et al. [42] also observed that the decomposition of CTPO starts at 250 °C. The second stage of decomposition is observed in the region of 200–275 °C. This is mainly due to destruction of intermolecular bonds and the weaker chemical bonds are destroyed results in the production of gaseous phase. The loss of weight percentage in CTPO is greater compared to CoTPO. The thermal decomposition of CoTPO starts at 350 °C, there follows mainly two losses called pyrolysis and devolatilization and complete by 550 °C and above which there is no further weight loss and the region characterized by carbon particles of constant weight [36]. The present studies reported that the decomposition temperature of CTPO, CoTPO and StTPO are 270, 320 and 330 °C, respectively. The study revealed that the CoTPO and StTPO shows much higher thermal stability than CTPO. Fig. 9 shows the thermogravimetric analysis of CTPO, CoTPO and StTPO respectively. TGA analysis of CTPO seems a drastic variation in comparison with CoTPO and StTPO. The major reason is due to the decomposition of crude oil triggered by the polar and acidic compounds. However, the upgraded oil (CoTPO and StTPO) showed much better thermal stability than CTPO.

3.8. Oxidation stability

The oxidation stability studies are carried out by keeping the crude and upgraded tire pyrolytic oil in a hot air oven at 120 °C for 20 h. The gummy deposits were found in CTPO due to the polymerization of olefins whereas the CoTPO looks unaltered and showed no changes during long term storage. Fig. 10 shows the oxidation stability studies of CTPO. The study depicts the existing problems in the industry for the long-term storage of oil. Besides, this will cause corrosion and deteriorate the pipelines in the industry. The upgraded oil (CoTPO and StTPO) has diesel like odor in comparison with the CTPO (sulfurous smell) due to excessive reduction in acidic contents and sulfurous compounds after upgradation. In addition to that, the storage and handling of CTPO is problematic due to the pungent odor and phase separation and olefin deposits during long term storage but there are no

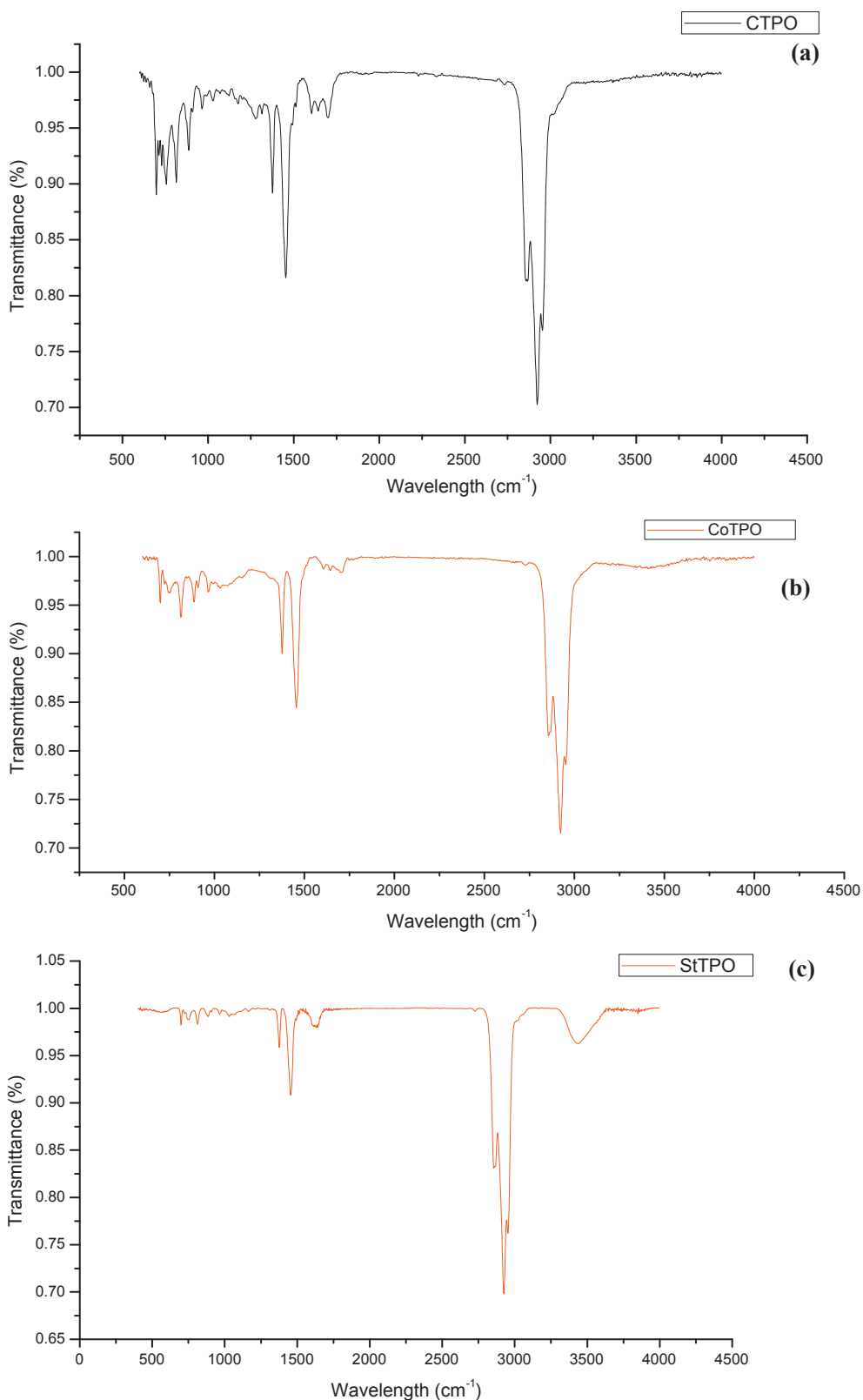


Fig. 6. FT-IR spectra of (a) CTPO, (b) CoTPO, (c) StTPO.

such issues with CoTPO and StTPO. There are no reported studies in the literatures about the oxidation stability of CTPO from pilot scale rotating autoclave reactor and CoTPO obtained using novel upgradation strategy.

3.9. Recovery and re-generation of used silica

The silica used during the upgradation process can be recovered by calcination. The calcination studies were carried out in a muffle furnace, which was maintained at a temperature of 800 °C. Fig. 11(a), (b)

Table 4
¹H NMR results of CTPO, CoTPO and StTPO.

Chemical shift (ppm)	Components	Percentage of total hydrogen in CTPO (mol%)	Percentage of total hydrogen in CoTPO (mol%)	Percentage of total hydrogen in StTPO (mol%)
3.2–0.9	Alkane or aliphatic	71.1	86.98	89.71
3–2	Aliphatic connected to aromatics	12.7	4.87	4
6.6–4.6	Olefins or Oxygenates	4.1	2.07	2.94
8.3–6.8	Aromatics	12.1	6.08	3.35
9.3	Aldehydes	0.1	–	–

Table 5
 Chemical composition of CTPO analyzed by GC–MS.

Molecular formula	Retention time (R.T)	Identified compounds	Peak area percentage (%)
C ₈ H ₁₀	4.9	1,3-Dimethyl benzene	2.99
C ₉ H ₂₀	5.35	<i>n</i> -Nonane	4.98
C ₁₀ H ₂₂	7.53	Decane	4.98
C ₁₀ H ₁₆	8.34	Limonene	7.60
C ₁₁ H ₂₄	9.66	Undecane	5.03
C ₁₂ H ₂₆	11.65	Dodecane	3.76
C ₁₇ H ₃₆	11.83	Tetradecane	0.24
C ₁₅ H ₃₆	11.97	<i>n</i> -Pentadecane	0.24
C ₁₆ H ₃₄	15.22	Hexadecane	4.11
C ₁₇ H ₃₆	16.66	Heptadecane	4.97
C ₁₇ H ₃₆	16.84	2,6,10-Trimethyltetradecane	3.37
C ₁₇ H ₃₆	17.06	2,6,10-Trimethyltetradecane	10.91
C ₁₆ H ₃₄ S	18.35	Tert-hexadecanethiols	0.33
C ₂₇ H ₅₆	19.81	Hepta-Cosane	5.31
C ₂₁ H ₄₄	21.24	Heneicosane	5.31
C ₈ H ₁₀	22.91	1,3-Dimethyl benzene	2.99
C ₉ H ₂₀	23.14	<i>n</i> -Nonane	4.98
C ₁₀ H ₂₂	25.17	Decane	4.98
C ₁₁ H ₂₄	27.57	Undecane	5.03

shows the scanning electron microscope (Jeol JSM-6380LA) images of pure silica, and recycled silica after calcination. The comparison of morphology of fresh and calcined silica gel reveals that the particles remain intact even after calcination at 800 °C in a muffle furnace and can be reused.

3.10. Economic analysis of lab scale upgradation strategy

Economic analysis is a function of capital cost, labour charges,

Table 6
 Chemical composition of CoTPO analyzed by GC–MS.

Molecular formula	Retention time (R.T)	Identified compounds	Peak area percentage (%)
C ₈ H ₁₀	6.05	Ethyl benzene	1.32
C ₈ H ₁₀	6.27	Ethyl benzene	1.32
C ₉ H ₉ BrO	6.77	Benzene propanoyl bromide	2.16
C ₁₂ H ₂₀ O ₂	7.67	Isopulegol acetate	1.31
C ₁₀ H ₁₆	8.06	Limonene	0.64
C ₉ H ₁₂	8.28	Benzene,1-ethyl-3-methyl	2.07
C ₁₀ H ₁₈ O	8.64	3,6-Ctadien-1-ol	2.92
C ₁₂ H ₂₀ O ₂	9.73	Cyclohexane	2.05
C ₁₂ H ₂₀ O ₂	10.88	6-isopropenyl-3-methoxymethoxy-3methyl-cyclohexane	1.70
C ₁₈ H ₂₈ O ₂	11.36	10,12-Ctadecadiynoic acid	10.83
C ₁₃ H ₁₈ O	12.32	Oxacyclotetradeca-4,11-diyne	1.30
C ₁₁ H ₁₄	13.19	Benzene,1-methyl-3-91-methyl-2-propenyl	4.20
C ₁₇ H ₂₄ O	15.57	Falcarinol	0.74
C ₁₄ H ₂₀	16.46	°Ct-3-ene-1,5-diyne	2.40
C ₁₈ H ₂₄ O ₂	17.44	5,8,11-Heptadecatriynoic acid, methyl ester	3.24
C ₁₈ H ₂₄ O ₂	17.95	5,8,11-Heptadecatriynoic acid, methyl ester	3.24
C ₁₃ H ₁₄	19.11	3-(2-Methyl-propenyl)-1H-indene	21.28
C ₁₈ H ₂₄ O ₂	19.39	5,8,11-Heptadecatriynoic acid	1.55
C ₃₃ H ₅₄ O ₃	20.89	Cholest-22-ene-21-ol,3,5-dehydro-6-methoxy	1.27

Table 7
 Chemical composition of StTPO analyzed by GC–MS.

Chemical Formulae	Retention time (R.T)	Compound	Peak area %
C ₇ H ₈	4.27	Toluene	0.84
C ₈ H ₁₀	6.17	Ethyl benzene	1.54
C ₉ H ₁₀	6.41	<i>p</i> -Xylene	2.33
C ₉ H ₁₀	6.99	<i>p</i> -Xylene	1.31
C ₉ H ₁₂	7.71	Benzene(1-methylethyl)	1.09
C ₁₂ H ₂₀ O ₂	8.08	Isopulegol acetate	0.60
C ₉ H ₁₂	8.55	Benzene, 1-methyl-3 methyl	1.25
C ₉ H ₁₂	8.83	Benzene, 1-methyl-3 methyl	2.02
C ₁₄ H ₂₀ O	9.25	Cyclopentanol, (1-methylene 2-propenyl)	1.60
C ₉ H ₁₂	9.7	Benzene, 1,3,5-trimethyl	11.85
C ₁₂ H ₂₀ O ₂	10.62	Cyclohexene 4-isopropenyl-1-methoxymethoxymethyl	11.85
C ₁₂ H ₂₀ O ₂	11.32	6-Isopropenyl-3 methoxymethoxy-3methyl-cyclohexene	1.70
C ₁₀ H ₁₆	12.08	3-Carene	1.70
C ₁₀ H ₁₂	12.3	Benzene, 4-ethenyl-1,2-dimethyl	0.65
C ₁₃ H ₁₈ O	13.91	Oxacyclotetradeca- 4,11-diyne	1.55
C ₁₁ H ₁₄	14.83	Benzene, 1-methyl-3-(1-methyl-2-propenyl)	0.51
C ₁₁ H ₁₄	15.05	Benzene, 1-methyl-3-(1-methyl-2-propenyl)	0.94
C ₁₇ H ₂₄ O	18.2	Falcarinol	1.52
C ₁₄ H ₂₀	19.36	°Ct-3-ene-1,5-diyne,3-t-butyl-7,7-dimethyl	41.39
C ₂₂ H ₃₂ O ₂	21.3	Retinol, acetate	1.40
C ₁₃ H ₁₄	22.83	3-(2-Methyl-propenyl)-1H-indene	1.06
C ₁₇ H ₃₆	25.31	Tetradecane-2,6,10-trimethyl	0.15
C ₁₅ H ₁₇ BrO	26.43	4a-10a-Methanophenanthren-9-β-ol,11- <i>syn</i> -bromo-1,2,3,4,4a,9,10,10a-°Ctathydro	0.91
C ₁₃ H ₁₆ N ₄ O ₆	40.52	2-Acetoxyptanal 2,4-dinitrophenyl hydrazine	0.57

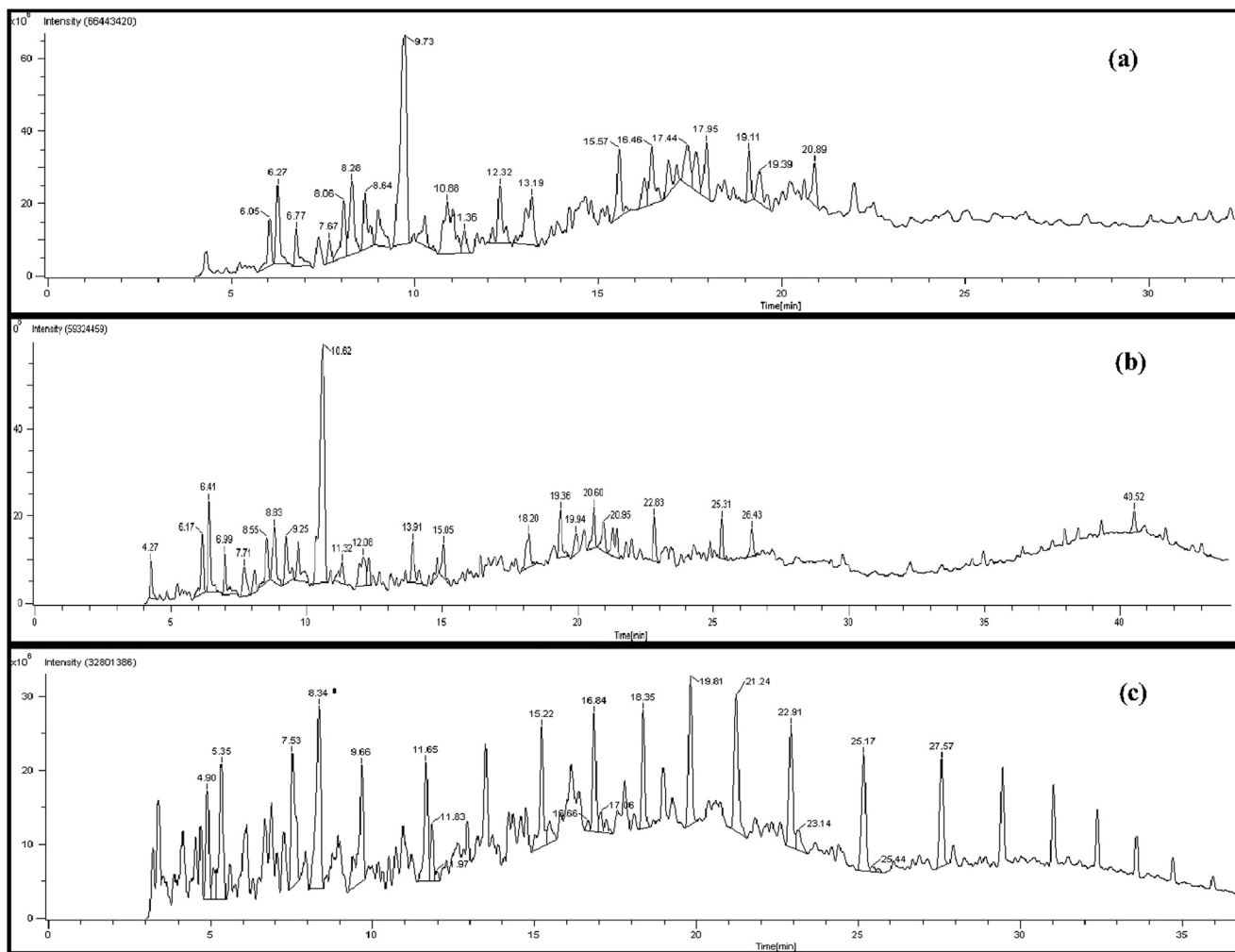


Fig. 7. GC-HRMS spectra of (a) CTPO and (b) CoTPO, (c) StTPO.

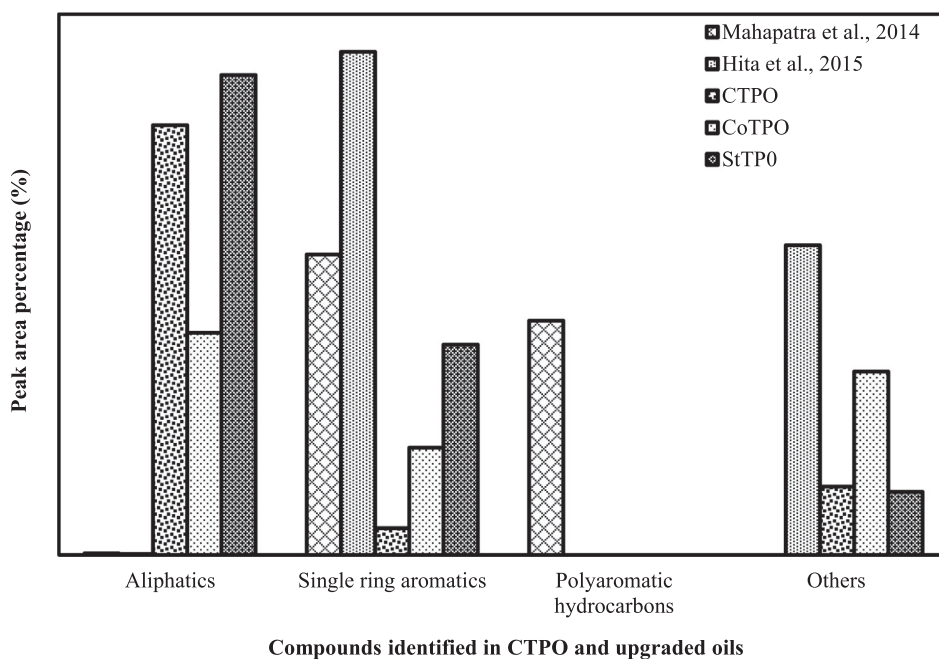


Fig. 8. Types of compounds in CTPO, CoTPO and StTPO.

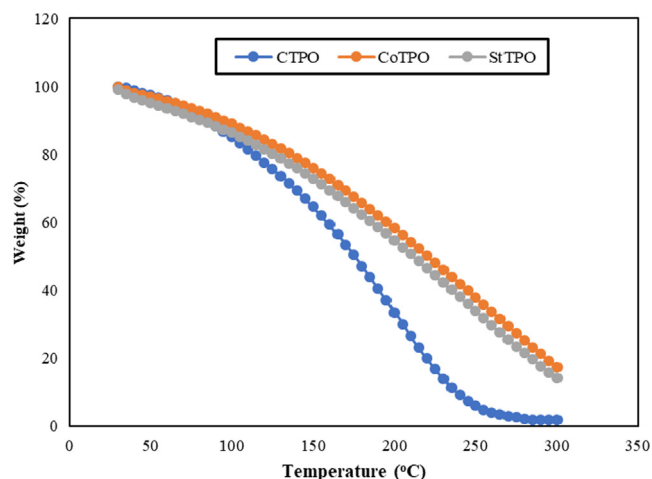


Fig. 9. TGA of CTPO, CoTPO and StTPO.



Fig. 10. Gummy deposits formed during storage of CTPO.

electricity, maintenance etc. The present strategy is purely based on lab scale strategy (1L). The economic analysis is calculated based on the consumable cost, power consumption and regeneration cost of solvent and adsorbent. The production cost of 1L upgraded oil (with regeneration) is found to be 0.33\$. Distillation is found to be more energy intensive [39] than present upgradation strategy using solvents and adsorbents. The detailed economic analysis of upgradation process with all factors are out of scope of the present study. The design of novel

upgradation strategy for industrial scale and the cost optimization of upgradation strategy will be planned in the future. Table 8 reports the cost of consumables used for the present upgradation strategy.

3.10.1. Electricity cost during heating and cooling

$[C_p = 0.90 \text{ kJ/kg K, Density of TPO} = 907 \text{ kg/mL, Yield from 1L CTPO} = 85 \text{ mL}]$

$$\text{Energy} = M * C_p * (T_1 - T_2) = (907 * 85) * 0.90 * (60 - 30) = 2081.56 \text{ kJ}$$

$$\text{Power} = 0.578 \text{ kW}$$

Cost of 1 kW electricity = 10 INR (Assumed)

Electricity cost for 0.578 Kw = 5.78 INR

3.10.2. Regeneration cost

Cost of heating silica gel at 800°C for 1 h = $M * C_p * (T_1 - T_2) = 1 * 1.13 * (800 - 30) = 870.1 \text{ kJ}$.

$$\text{Power} = 870.1 / 60 * 60 = 0.2416 \text{ kW}$$

Prices is assumed to be 10 INR for 1 kW

Electricity cost needed for heating used-silica = 2.416 INR

Total regeneration cost = 2.416 INR (0.034 \$)

Laboratory scale production cost per 1L Upgraded Tire pyrolysis oil with regeneration = INR 15.40 + INR 5.78 + INR 2.416 = **INR 23.596 (0.33 \$)**

3.10.3. Energy required for distillation of CTPO

$$E = M * C_p * (T_1 - T_2) = (907 * 95) * 0.90 * (400 - 75) = 25203.26 \text{ kJ,}$$

$$\text{Power} = 7.00 \text{ kW.}$$

3.11. Scale-up strategy of upgraded TPO

A limitation of the current lab-scale batch strategy is the physical loss of upgraded oil during filtration through a filter paper and separation from the adsorbent (i.e. silica gel). The reaction was scaled up in a batch reactor fitted with an overhead magnetic stirrer. After reaction, the mixture was passed through an efficient membrane-based filtration system to remove silica gel particles (Fig. 12). Silica gel was also washed by petroleum ether to minimize physical hold up of TPO. The collected solution of upgraded TPO in petroleum ether was connected to a rotary evaporator and petroleum ether was distilled out under controlled vacuum. Preliminary studies show that using a larger scale of crude TPO (5 L) and a membrane-based filtration system significantly lowered the loss of upgraded TPO to 5% only compared to

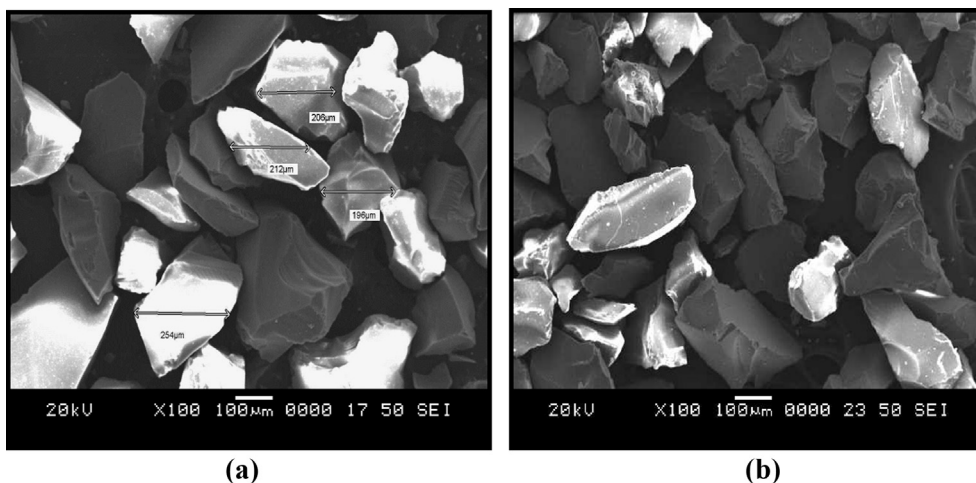


Fig. 11. Scanning Electron microscopy of (a) silica gel and (b) calcined silica.

Table 8

Cost of consumables in the upgradation strategy.

Particulars	Cost/Metric ton	Quantity	Cost/Kg	Recovery (%)	Cost/ liter
Silica gel (60–120 mesh)	70,000	1 kg	70	90	7.00
Petroleum ether (60 °C–80 °C)	42,000	2 L	42	90	8.40
Estimated consumables cost (INR)					15.40

15% in the lab-scale. Alternatively, the upgrading can also be carried out and scaled up in a continuous regime. The solution of CTPO and petroleum ether can be pumped through columns packed with silica connected in series. The contact time of TPO with silica gel can be modified by monitoring the rate of flow and/or the number of columns used in the experiment. When one or more columns are exhausted, they can be replaced with new columns and the used silica gel can be recycled by calcination. The petroleum ether solvent can be recycled by atmospheric or vacuum distillation as described in the batch strategy.

3.12. Conclusion

CTPO obtained from a rotating autoclave reactor has been upgraded by using silica gel as a selective adsorbent and petroleum ether as a diluent. Both crude and upgraded oils were studied extensively on their chemical composition and fuel properties. The results show that silica gel effectively removed oxygenates, nitrogen and sulfur containing

compounds responsible for inferior fuel properties of CTPO. As a result, the fuel properties of the upgraded oils improved significantly and match closely with diesel fuels. Mechanically stirring CTPO with silica gel was found to be more effective in removing polar compounds when compared to passing through a column of silica gel that can be explained by longer contact time of CTPO with silica gel in the former strategy.

Conflicts of interest

The authors declare no conflict of interest.

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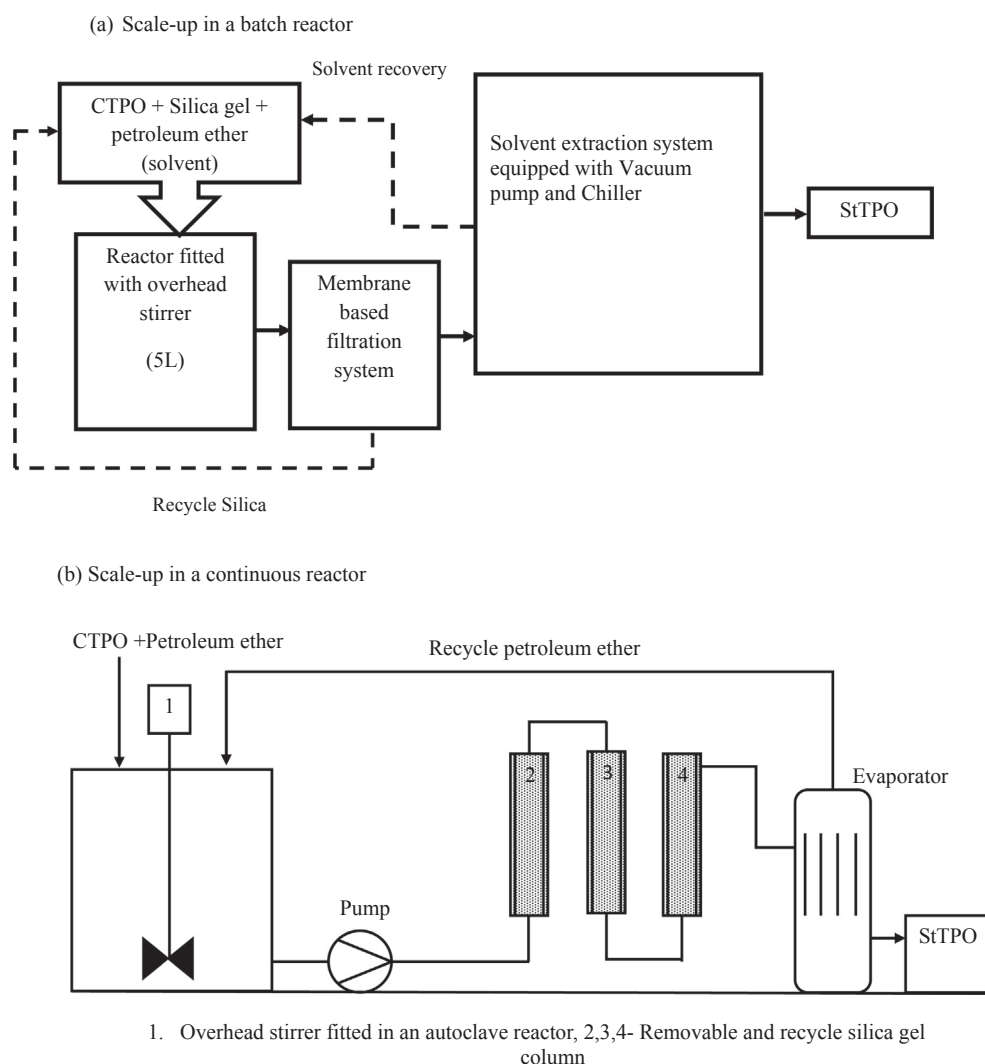


Fig. 12. Scale up strategy of upgraded TPO in (a) batch and (b) continuous regime.

data. The authors also thank Mandakan Energy Products, Palakkad, Kerala for supplying CTPO free of cost and allowing to perform pyrolysis experiments at their facility. Akhil Mohan thanks National Institute of Technology Karnataka, Surathkal, India for scholarship support.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fuel.2019.03.139>.

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