

Kinetic Studies on Extraction of Oil from a New Feedstock (Chukrasia Tabularis L. Seed) for Biodiesel Production and Optimizing the Process Using a Heterogeneous Catalyst

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Abstract

In this study, *Chukrasia tabularis* L. (*C. tabularis*) seed is identified as a new feedstock for biodiesel production. The seeds are pretreated by autoclave assisted ultrasonic homogenization process (AUH) and an appropriate solvent was chosen to extract the total oil content. The oil extracted from the seed was maximum for n-hexane (32 wt%). Further, the kinetic and thermodynamic studies are performed in batch extraction using n-hexane. The data shows that the extraction follows first order kinetics and further, their rate constants, thermodynamic parameters and activation energy were calculated. Finally, the physiochemical properties of the oil are estimated using standard methods. It is identified that *C. tabularis* oil has high free fatty acid (FFA). Hence, it requires an acid catalyst to catalyze a single step, both esterification and transesterification simultaneously to produce biodiesel. The heterogeneous acid catalyst (HAC) has numerous advantages compared to a homogeneous catalyst. In this work, HAC is synthesised from a carbon precursor by a chemical reduction and activation process. Moreover, its physiochemical properties are characterised and used to catalyze the biodiesel production process. The optimum oil conversion was 99.2% at 6 wt% catalyst loading, 15:1 methanol to oil molar ratio, 120 min reaction time, 70 °C reaction temperature and 500 rpm stirring rate. The physiochemical characteristics of biodiesel were determined using standard methods and compared with the ASTM D6751 standard.

1. Introduction

Worldwide, society needs emerging energy resources and safeguarding the environment from pollution (Berrios et al. 2009). Biodiesel is one of the prominent energy sources with non-polluting and biodegradable characteristics. This insists that various researches on biodiesel make it commercially viable and affordable for all classes of people. Biodiesel consists of alkyl esters produced from triglyceride sources with either one of the short-chain alcohols. The main triglyceride providing sources are vegetable oils, waste /reused cooking oils, animal/poultry waste tallows, low valuable fat materials, etc. The commercialization of biodiesel is greatly hindered by the raw material cost required to produce high quality biodiesel (Ozturk et al. 2010). Hence, the underutilized plant sources are examined to obtain a suitable feedstock of triglycerides.

The investment cost of raw materials contributes around half of the total expenses in the biodiesel industry (Demirbas 2009). Non-edible plant oils were chosen over edible plant oils as a possible source of biodiesel. *C. tabularis*, also called as Indian mahogany. It is a medium to large deciduous or evergreen non-edible oil yielding tree native to India, Bangladesh, Cambodia, China, Srilanka, Vietnam and Malaysia (Ibrahim et al. 2018). This tree's stem, leaves and fruits have antioxidant, antimalarial and antiviral properties. Seeds are 60–100 per locule, fat 1–2 cm long with brown suede wing twice the remaining portion length of the seed. Cotyledons were thin, radicle facing the wing and the endosperm was not present (Mursiti et al. 2019). Seeds do not have much pharmaceutical importance; thus, they could be looked at as a suitable source for biodiesel production. From the literature review, it is identified that *C. tabularis* was rarely studied for biodiesel production. In this study, *C. tabularis* oil was selected as a vital

source for biodiesel production. The higher biodiesel conversion was directed by optimizing process parameters to scrutinize reaction conditions.

Alkyl esters, in particular fatty acid methyl esters (FAME), are the main product of the reaction between triglycerides and methanol, along with glycerol as a byproduct. Transesterification has been accepted as the comfortable pathway to convert long-chain fatty acids in triglycerides to alkyl esters (Demirbas 2009). Usually, the reaction rate is increased by the addition of a catalyst. The acidic and basic nature of the catalyst was chosen based on the nature of the feedstock. Homogeneous catalysts (KOH, NaOH, CaO, CaOH, H₂SO₄, etc.) were reported as effective catalysts for a higher yield of biodiesel (Kalam et al. 2008). However, the reaction needed post-treatment processes like washing and catalyst separation. Excessive water requirement for the washing was the primary downside of homogeneous catalyst. Also, the biodiesel produced had disliked properties like corrosiveness, degradability and change of physiochemical properties. This led to the development of various combinations of acidic and basic heterogeneous catalysts (Sivakumar et al. 2013).

In this work, *C. tabularis* oil was extracted from AUH treated *C. tabularis* seeds and different solvents were used for extraction to identify the maximum oil yield. Further, the kinetics and thermodynamic studies were performed for the batch extraction process to calculate the rate constant and thermodynamic properties. The chemical reduction and activation process was used to synthesize heterogeneous acidic catalyst from the catalyst precursor. Moreover, the synthesized catalyst was characterized using scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET) analysis, Boehm titration method and Fourier transform infrared spectroscopy (FTIR) and subjected to catalyze biodiesel process (Saka 2012). The parameters affecting the process were optimized. Finally, the biodiesel was analyzed by FTIR, proton nuclear magnetic resonance (¹HNMR) spectroscopy and the fuel properties were investigated by the standard methods and compared with ASTM D6751 standard.

2. Materials And Methods

C. tabularis seeds were purchased from a local nursery shop in Chennai, India. The chemicals and solvents used were of laboratory grade. Anhydrous sodium sulphate and 98.4% conc. H₂SO₄ were purchased from Sisco Research Laboratories in Mumbai, India. Methanol, ethanol, n-hexane, petroleum ether, chloroform and acetone were purchased from Merck in Mumbai, India. Commercial activated carbon (catalyst precursor), hypo-phosphorous acid, sulphanilic acid and sodium nitrite were purchased from Vijaya Scientifics in Chennai, India. All the chemicals and solvents are used as such without any processing.

2.1. Feedstock Preparation

C. tabularis seeds were removed from locules by hand separation and cleaned from plant debris. The seeds were dried at 95 °C in a hot air oven until a constant weight was obtained and it was powdered

using a laboratory crusher. Subsequently, it was passed through ASTM 10 mesh and stored in a desiccator.

The AUH pretreatment was used to loosen up the endosperm cells in the seed. It was done by autoclaving the powdered feedstock at 121 °C for 15 min under 15 psi in a closed beaker. Further, it was suspended in a selected solvent medium and ultra-sonicated at 20 kHz using probe-type Z511463-1 EA sonicator (Merck, USA) for 40 min. It was highly intense and effective (Vishnupriya et al., 2019). The sonicator was operated at 500 W with 20% amplitude and duty cycle at 20 s ON: 20 s OFF. Finally, the solvent was separated using a rotary vacuum evaporator.

2.2. Estimation of Total Oil Content

To find the total oil content in the seeds, extraction was carried out in a 300 mL Soxhlet extractor connected with a condenser. An accurately weighed sample of 20 g was placed in the thimble, which was kept inside the extractor. The extraction process was carried out for 6 h using the feedstock before and after AUH treatment. Moreover, the appropriate solvent that can be used to extract maximum oil content was determined for four different solvents like n-hexane, petroleum ether, chloroform and acetone. When the extraction was completed, the solvent was separated by simple distillation and the oil yield was determined as per Eq. (1) in weight percentage.

$$\text{Oilyield}(wt\%) = \frac{\text{Extracted oil weight}(g)}{\text{Feedstock weight}(g)} \times 100$$

1

2.3 Kinetic and Thermodynamic Studies

The kinetic and thermodynamic studies were performed using the selected solvent in a batch extraction process. The appropriate quantity of solvent was mixed with feedstock and extraction was carried out in a 500 mL double-neck flat bottom flask. The central neck was connected with a reflux condenser to reflux the evaporated solvent. The setup was placed on a magnetic stirrer, which is operated at a fixed 300 rpm stirring rate. The parameters such as solvent to feedstock ratio, extraction temperature and extraction time were varied to find the optimum conditions.

2.4 Characterisation of *C. tabularis* Oil

The physiochemical properties of *C. tabularis* oil sample were analyzed as per the standard methods following Official Methods and Recommended Practices (2004). The fatty acid composition of the *C. tabularis* oil sample was quantified and qualified using QP2010 PLUS gas chromatography (GC) (SHIMADZU, Japan). The system has a 60 m capillary column, especially for separating volatile organic components. Nitrogen was used as carrier gas with a flow rate of 0.95 mL min⁻¹, whereas the ignition chamber was supplied with oxygen and hydrogen. The injection and detection port column temperatures were maintained at 280 and 250 °C, respectively (Arumugamurthy et al. 2019). The samples required for GC analysis were prepared by following the Boron trifluoride-Methanol methylation procedure

(Booramurthy et al. 2022). A measured sample (1 μ L) was injected into the column. In the beginning, the oven temperature was 50 $^{\circ}$ C and raised at the rate of 7.5 $^{\circ}$ C with 2 min holding time. The final oven temperature was around 300 $^{\circ}$ C. Win-Chrom software was used to collect the data and compared it with the retention time of 37 FAME obtained from Sigma-Aldrich Chemicals Pvt. Ltd in Bangalore, India (18919-1AMP, FAME Mix). The resulting integral peak areas and the retention time were used to interpret the quantity and quality of FAME. The mean molecular weight of the oil was calculated by the data obtained from fatty acid composition using Eq. (2),

$$MW_{oil} = 3 \times \sum_{i=0}^n (MW_i X_i) + 38$$

2

where: MW_{oil} is the average molecular weight of oil; MW_i is the molecular weight of individual fatty acid present in oil and X_i is the percentage of individual fatty acid present in the oil.

The FTIR PerkinElmer Spectrum Two (PerkinElmer inc., USA) was involved in identifying the functional groups present in *C. tabularis* oil, HAC and its biodiesel. The spectrum of the samples were taken between 4000 and 400 cm^{-1} using a universal diamond attenuated total reflectance sampling tool. Subsequently, the baseline corrections obtained in the data were processed using PerkinElmer spectrum 10.4.2 software (Booramurthy et al. 2020).

The ^1H NMR spectrum for *C. tabularis* oil and biodiesel were recorded using Avance III 500 MHz spectroscopy (Bruker, Germany) using 5 mm probe head and deuterated chloroform as a solvent. The data were interpreted using TOPSPIN software. The method applied for quantification is based on the principle that the proton amplitude signals of nuclear magnetic resonance are directly proportionate to the hydrogen nuclei count present in the molecule. The ^1H NMR peak area depends on protons count and is independent of the respective response factor (Hariram and Vasanthaseelan 2016). The integral value of protons in the methylene radical adjoining ester moiety at 2.34 ppm in triglyceride and the alcohol moiety at 3.63 ppm in FAME is calculated from Eq. (3),

$$\text{Conversion}(\%) = \frac{2A_{ME}}{3A_{(\alpha-ME)}} \times 100$$

3

where: $A_{(ME)}$ is the integration value of FAME's methoxy protons and $A_{(\alpha-ME)}$ is related to the integration value of methylene protons.

2.5 Catalyst Synthesis

Chemical reduction of aryl diazonium salts functionalized catalyst precursor was found to be an efficient HAC besides general sulfonation and carbonization of polycyclic aromatic hydrocarbons (Liu et al. 2010).

Commercial activated carbon has been industrially proved as excellent catalyst support and environmentally applied for its chemical inertness, high specific surface area and inexpensive (Rodríguez-Reinoso 2001). Hence, it was chosen as a catalyst precursor. The initial step was the preparation of 4-benzene diazonium sulphonate (diazonium salt) followed by the functionalization of the catalyst precursor.

The diazonium salt was prepared from the sulphanilic acid by the diazotization reaction. In a double-neck round bottom flask, sulphanilic acid (13 g) was mixed in 1 M HCl (75 mL). The temperature was maintained between 0 and 5 °C in an ice-water bath and 1 M sodium nitrite (83 mL) was added dropwise into the chemical mixture. The mixture was stirred for 50 min. The resulting white precipitate of diazonium salt was filtered through a Whatman filter paper and rinsed using cold water to remove water soluble by products (Liu et al. 2010).

The functionalization of catalyst precursor (2 g) was carried out by mixing it with distilled water (100 mL), ethyl alcohol (100 mL) and diazonium salt (12 g) in a double-neck flat bottom flask. The hypophosphorous acid (200 mL) was added to the mixture in two parts at a time interval of 30 min. Further, the mixture was continuously stirred at 750–800 rpm for 30 min. The sulfonated solid acid catalyst was washed with distilled water until wash water became neutral, followed by acetone wash. Finally, HAC was dried at 95 °C till a constant weight was obtained (Prabhu et al. 2015).

2.6. Catalyst Characterisation

The topography of the HAC was obtained using SEM analysis (Carl Zeiss Evo-18, UK). The surface area, pore volume and pore diameter of the catalyst precursor and HAC were analysed by nitrogen adsorption and desorption isotherm method in a Micrometrics BET analyzer (ASAP2020, Georgia). The acid site density for catalyst precursor and HAC were determined using the Boehm titration method (Arumugamurthy et al. 2019). The surface carrying acid functional groups were quantified by titrating with a 0.1 N stock solution of sodium hydroxide, sodium carbonate, sodium bicarbonate and hydrochloric acid. 1 g of HAC was mixed with 50 mL of each stock solution and stirred for 24 h. The mixture was filtered to remove the retentate and the filtrate was titrated with 0.1 N hydrochloric acid. Sodium bicarbonate solution neutralizes carboxylic acid during titration, whereas sodium carbonate solution neutralizes both carboxylic acid and lactonic groups (saturated and unsaturated lactones). Similarly, phenolic groups, carboxylic acid and lactonic groups were neutralised by sodium hydroxide. The difference between the concentrations are used to identify the strong and weak acid sites (Kang et al. 2017).

2.7. Single Step Esterification and Transesterification Reaction

The reaction between *C. tabularis* oil and methanol was performed in a batch composed of a 300 mL double-necked flat bottom flask connected to a water-cooled condenser to reflux methanol back to the reactor. The setup was placed on a temperature-controlled magnetic stirrer. The temperature was

maintained with an accuracy of ± 1 °C. 50 mL of *C. tabularis* oil was filled in the reactor with a known quantity of catalyst and methanol. After completion of the reaction, the mixture was cooled and centrifuged at 3000 rpm for 30 min. After centrifugation, three layers were formed in which catalyst was found at the bottom below the glycerol layer and the top layer having biodiesel with excess methanol. The top layer is separated and the excess methanol present in the biodiesel layer was removed by a rotary vacuum evaporator. The different parameters influencing the process, such as catalyst loading from 3 to 7 with an increment of 1 wt%. The stoichiometric ratio of 3:1 methanol to oil is required for the reaction. Since the reaction is reversible, excess methanol is added to shift the reaction to the right. In this study, 3:1 to 18:1 methanol to oil molar ratio was performed. To find the optimum temperature, the temperature is varied between 40 and 70 °C. The maximum temperature was fixed as 70 °C which is the boiling point of methanol. Similarly, the reaction time and stirring rate were varied from 30 to 120 min and 300 to 600 rpm, respectively. To optimise different parameters, one factor at a time method was followed (Senthilkumar et al. 2019).

3. Results And Discussion

3.1. Solvent Selection

The oil yield for the different solvents is shown in Table 1. The appropriate solvent was chosen based on the maximum total oil yield. Among the solvents, the oil yield was obtained maximum for n-hexane (32 wt%), whereas for acetone, it was minimum due to its polar behaviour. When comparing the oil yield before and after pretreatment, it was confirmed that the pretreated feedstock gives a higher yield for all the solvents. This was due to the disruption of impermeable cell walls that induce solvent penetration, which increases the maximum oil yield. The pretreatment enhances the mass transfer gradient in solvent extraction (Vishnupriya et al. 2019).

Table 1
Yield of oil with respect to different solvents

Solvent	Oil yield (wt%)	
	without AUH	with AUH
n-hexane	27.9	32
Petroleum ether	27.7	30
Chloroform	24	26
Acetone	15	15.2

3.2. Optimization in Batch Extraction

3.2.1 Feed to solvent weight ratio

The solvent n-hexane was chosen due to its maximum oil yield. The weight ratio of feed and n-hexane decided the optimum solvent quantity required for batch solid-liquid extraction. Feed to solvent weight ratio was varied between 1:10, 1:15, 1:20 and 1:25. The extraction was carried out at 50°C for a constant time 90 min in a double-neck flat bottom flask with reflux. Figure 1 shows the oil yield for different feed to solvent weight ratios. The ratio of 1:20 was observed as an optimum with a maximum oil yield of 28.5 wt%. Further increase in weight ratio, the oil yield was approximately constant since the extraction reached equilibrium.

3.2.2 Effect of temperature on oil extraction

The oil was extracted at different temperatures at 1:20 feed to solvent weight ratio for 90 min. From Fig. 2, it was observed that the oil yield increases with an increase in temperature. The maximum oil yield of 29.3 wt% was obtained at an optimum temperature of 60°C. Further increase in temperature above 60°C led to slightly decreased oil yield which may be due to the phase change of solvent from liquid to vapour, making improper contact between solid and liquid phase.

3.2.3 Effect of extraction time

The effect of extraction time on oil yield was optimised at 1:20 feed to solvent weight ratio for 60°C. It was observed that the oil yield increases with an increase in extraction time. A similar trend was observed by other researchers also (Sivakumar et al. 2012; Ahmad et al. 2014). The optimum extraction time of 120 min with a maximum oil yield 31.2 wt%, as shown in Fig. 3. Further, increase in time did not show any significant yield. Moreover, the longer time duration leads to more consumption and energy and process delay.

3.3 Oil Extraction Kinetics and Thermodynamics

The AUH treated feed was weighed and taken in a 500 mL double-neck flat bottom flask connected with reflux was filled with 1: 20 optimum feed to solvent weight ratio. The extraction was performed at different time intervals and temperatures. The maximum oil extracted was obtained as 31.2 wt% at 60 °C in 120 min and the oil yield percentage represented 97.5% when compared to the total oil content in *C. tabularis* seed. The extraction rate constants of oil yield using n-hexane at various temperatures are listed in Table 2. A rate equation for *C. tabularis* oil extraction was shown in Eq. (4)

$$\frac{dY}{dt} = kY^n$$

4

where: Y is the percentage yield of oil; t is extraction time; k is the rate constant and n is the extraction order. Since there is an increased oil yield percentage with an increase in time, the term $\frac{dY}{dt}$ was positive (Al-Widyan and Al-Shyoukh 2002). The oil yield was calculated from assorted time and temperature

intervals by applying the differential method. The graph of $\ln \frac{dY}{dt}$ versus $\ln Y$ was plotted and linearity of equation fitting was found. The order of the extraction 'n' was calculated from the slopes of the straight lines which confirms the extraction follows first order kinetics and the extraction rate constants (k) were calculated.

Table 2

Extraction rate constants at different temperatures

Temperature (°C)	k (min ⁻¹)	'n' order	R ²
40	1.8x10 ⁻⁵	0.99	0.97
50	5 x10 ⁻⁵	0.98	0.93
60	1.4 x10 ⁻⁴	1.01	0.99
70	2.9x10 ⁻⁴	0.97	0.95

3.4 Calculation of Activation Energy

The rate constant increases with an increase in temperature was observed. The temperature dependence on extraction rate was stated using the Arrhenius Eq. (5),

$$k = Ae^{\frac{-E_a}{RT}}$$

5

where: k is the rate constant; A is the pre-exponential factor; E_a is the activation energy; R is the universal gas constant and T is the absolute temperature.

Figure 4 shows the plot of $\ln k$ versus T^{-1} give a straight line whose slope is the activation energy of extraction ($-E_a/R$) and the intercept ($\ln A$). The calculated activation energy and pre-exponential factors are 63.604 kJ mol⁻¹ and 66.66x10⁴ s⁻¹, respectively.

3.5 Thermodynamic Activation Parameters

The activation parameters ($\Delta S^\ddagger$, $\Delta H^\ddagger$ and $\Delta G^\ddagger$) for *C. tabularis* oil extraction were calculated using transition state theory as given in Equations (6), (7) and (8).

$$A = \frac{Rt}{Nh}e^{\frac{\Delta S^\ddagger}{R}}$$

6

$$\Delta H^\ddagger = E_a - RT$$

7

$$\Delta G^\ddagger = \Delta H^\ddagger - \Delta TS^\ddagger$$

8

where: N is the Avagadro's number; h is the Planck's constant; $\Delta S^\ddagger$ is the activation entropy; $\Delta H^\ddagger$ is the activation enthalpy and $\Delta G^\ddagger$ is the activation Gibb's free energy. The calculated activation thermodynamic parameters at different temperatures are given in Table 3.

Table 3
Thermodynamic activation parameters of *C. tabularis* oil extraction

Temperature (K)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta G^\ddagger$ (kJ mol ⁻¹)
313	-133.82	61.00	102.88
323	-134.08	60.92	104.23
333	-211.30	60.84	131.20
343	-211.55	60.75	133.31

3.6 Thermodynamic parameters

The thermodynamic parameters such as the change of enthalpy, the change of entropy and the Gibb's free energy (ΔH , ΔS and ΔG) for the *C. tabularis* oil extraction can be calculated using the following Equations (9) and (10) as suggested by Topallar and Geçgel 2000.

$$K^* = \frac{Y_T}{Y_u}$$

9

$$\ln K^* = - \frac{\Delta G}{R} \frac{1}{T} = - \frac{\Delta H}{R} \frac{1}{T} + \frac{\Delta S}{R}$$

10

where: K^* is the equilibrium constant; Y_T is the oil yield percentage (wt%) at different temperature for 120 min; T is the absolute temperature and Y_u is the un-extracted oil percentage (wt%).

The plot was drawn for $\ln Y_T$ versus T^{-1} in which the slope represents ΔH and was calculated as 93.54 kJ mol⁻¹ as shown in Fig. 5. The enthalpy obtained was positive, signifying that the oil extraction process is endothermic and requires energy input throughout the process.

The thermodynamic parameters and the equilibrium constant in oil extraction are given in Table 4 for different temperatures. The entropy change increases with an increase in temperature and the value of free energy is negative ($\Delta G < 0$). The decrease in value with respect to temperatures confirms *C. tabularis* oil extraction using n-hexane is a spontaneous process. The positive value of entropy change ($\Delta S > 0$) indicates the extraction is irreversible.

Table 4

Equilibrium constants and thermodynamic parameters

Temperature (K)	K^*	ΔG (kJ mol ⁻¹)	ΔS (mol ⁻¹ K ⁻¹)
313	1.78	-1.500	5.09
323	10.55	-6.331	19.88
333	15.42	-7.573	23.02
343	15.55	-7.825	23.10

3.7 Physiochemical Characterisation of *C. tabularis* Oil

The oil extracted was deep yellow in colour. The total oil content was 32 wt% and its physiochemical properties are enclosed in Table 5. The acid value of the oil was higher which suggest the use of an acid catalyst to convert FFA to FAME. The saponification value was found to be 267.8 mg KOH g⁻¹ of oil which was higher when compared to other vegetable oils representing the presence of short-chain fatty acids. The iodine value of *C. tabularis* oil was 104.05 g of iodine absorbed per 100 g of oil, categorized under drying oil. This value leads to a susceptibility of polymerization and oxidation when exposed to air and decreases the storage stability of this oil. To overcome these issues, the biodiesel produced from this oil requires antioxidants.

The fatty acid composition of *C. tabularis* oil is given in Table 6, representing that the unsaturated fatty acids are in a higher percentage. The oil has 18.73% saturated fatty acids, 47.7% monounsaturated fatty acids and 31.82% polyunsaturated fatty acids. The total average molecular weight of oil was calculated as 859.95 g mol⁻¹. The degree of unsaturation was found to be around 64.31. This value suggests that the percentage of unsaturated fatty acids (oleic acid and linoleic acid) are higher. Hence, the oil is in the liquid state at room temperature (Fameau et al. 2014). The biodiesel produced from the oil has better cold flow properties and less emission of NO_x during combustion (Hazrat et al. 2020). Subsequently, the optimal fuel quality of *C. tabularis* biodiesel can be achieved by blending it with other biodiesels having higher saturated fatty acids (Gopinath et al. 2015). The calculated value of the mass ratio of saturated to unsaturated fatty acids was less than 1, representing the biodiesel has a cetane number and calorific value slightly lesser than other biodiesel (Demirbas 2009).

Table 5
Physiochemical properties of *C. tabularis* oil

Properties	Values
Density (g cm ⁻³)	0.862
Viscosity @ 40°C (mm ² s ⁻¹)	30.15
Water content (wt%)	0.05
Acid value (mg KOH g ⁻¹)	30
Saponification value(mg KOH g ⁻¹)	267.8
Iodine value (g I 100 g ⁻¹)	104.05
Average molecular weight (g mol ⁻¹)	859.95
Degree of unsaturation	64.31

Table 6
Fatty acid composition of *C. tabularis* oil

Fatty acid	Structure	Composition (%)
Caprylic acid	C8:0	0.47
Capric Acid	C10:0	0.44
Myristic acid	C14:0	2.31
Palmitic acid	C16:0	14.83
Arachidic acid	C20:0	0.68
Phthalic acid	C8:2	0.65
Terephthalic acid	C16:4	1.00
Oleic acid	C18:1	47.19
Linoleic acid	C18:2	16.45
Linolenic acid	C18:3	13.26
Gadoleic acid	C20:1	0.51
Arachidonic acid	C20:4	0.46
Undetectable	–	1.75

3.8 HAC Characterisation

The values in Table 7 evidenced that the surface area from the BET method decreased from 751 to 602 $\text{m}^2 \text{g}^{-1}$ after the reduction process representing the embedment of $-\text{SO}_3\text{H}$ on the plane surface of the catalyst precursor. There was a considerable reduction in pore volume from 0.47 to 0.38 $\text{cm}^3 \text{g}^{-1}$ and pore diameter was reduced from 2.5 to 2.3 nm. The strong and weak acid distribution among catalyst precursor and HAC were listed in Table 7, where the strong acid site distribution is high in HAC, which represented the occupancy of $-\text{SO}_3\text{H}$ on the catalyst precursor.

Table 7
Surface area analysis and acid site density of catalyst precursor and HAC

Sample	Surface area (m^2g^{-1})	Pore volume (cm^3g^{-1})	Pore diameter (nm)	Strong acid site density (mmolg^{-1})	Weak acid site density (mmolg^{-1})	Total acid density (mmolg^{-1})
Catalyst precursor	751	0.47	2.5	0.01	0.12	0.13
HAC	602	0.38	2.3	0.77	0.25	1.02

The topography of catalyst precursor and HAC were analyzed by SEM. Figure 6(a) represents the catalyst precursor before the reduction process with an amorphous and smooth structure having the pore diameter of 2.5 nm and the pore volume of 0.47 cm^3g^{-1} . Whereas, Fig. 6(b) represents the HAC synthesised by the chemical reduction process, showing a scaly and irregular structure in which the pore diameter is reduced to 2.3 nm and the pore volume reduced to 0.38 cm^3g^{-1} due to the surface intrusion of acid groups on the catalyst precursor (Guo and Lua 1999).

The FTIR spectra of chemically reduced sulfonated HAC is shown in Fig. 7. It was evident that the $-\text{SO}_3\text{H}$ group was formed on the surface of the HAC which is represented by the peaks formed at 1173 and 1126 cm^{-1} representing the presence of an asymmetric stretching vibration peak of $\text{O}=\text{S}=\text{O}$. Similarly, peaks observed at 1158 and 665 cm^{-1} correspond to symmetric stretching vibration peak of $\text{O}=\text{S}=\text{O}$ and stretching vibration peak of $\text{C}-\text{S}$ where hydrogen is bonded with $-\text{SO}_3\text{H}$, respectively (Kang et al. 2017). The vibration band located at 1628 cm^{-1} is attributed to the stretching vibration modes of sulfate groups (Prabhu et al. 2015). The peaks at 2923 and 2856 cm^{-1} indicate the presence of both methylene ($-\text{CH}_2-$) bridges and aromatic C-H stretching vibrations respectively. Absorption peak at 1400 cm^{-1} indicates the presence of aromatic $\text{C}=\text{C}$ groups stretching vibrations in alcohols, phenols or ether or ester groups. Whereas, the presence of group $\text{C}-\text{O}-\text{H}$ was assigned to an absorption peak at 865 cm^{-1} (Chafidz et al. 2018). The band at 1700 cm^{-1} denotes the existence of carbonyl/carboxyl groups of $-\text{COOH}$ (Saka 2012). The produced HAC have both carboxylic acid and sulfonic acid sites. Hence, the presence of both the functional groups will improve acid site density that could enhance the FAME production.

3.9 Optimisation of Biodiesel Production

3.9.1 HAC loading

Figure 8(a) shows that investigated effect of HAC loading on biodiesel production. The catalyst amount is one of the main parameters that need to be optimised to increase the FAME conversion. From a previous report, it was found that the minimum heterogeneous catalyst required required for optimum biodiesel production as 3 wt% (Kay and Yasir 2012; Theresa et al. 2017). In this study, the HAC quantity varied from 3 to 7 wt% and its effect was studied. Due to insufficient active sites, the low value of catalyst loading could not give maximum FAME conversion. In contrast, the excess loading of the catalyst leads to disturbing the equilibrium (Munir et al. 2021). The optimum HAC weight was found to be 6 wt%, for which a maximum conversion of 79% was obtained.

3.9.2 Methanol to *C. tabularis* oil molar ratio

It was observed that the conversion of FAME is greatly affected by the methanol to *C. tabularis* oil molar ratio, as shown in Fig. 8(b). According to stoichiometry, three moles of methanol are required for one mole of triglyceride (Hoda 2010). But excess moles of methanol directed the reaction flow by shifting the equilibrium towards FAME formation (Roy et al. 2020). The methanol to *C. tabularis* oil molar ratio was varied and investigated. When the molar ratio was increased from 3:1 to 15:1 the conversion percentage increased from 22 to 87%. Further, an increase in molar ratio does not affect significant improvement conversion. Excess methanol above the optimum dosage increases glycerol solubility, which interferes with glycerol separation. Moreover, the soluble glycerol shifts the reaction backward, which reduces the conversion of FAME (Pasupulety et al. 2013).

3.9.3 Reaction temperature

The reaction temperature was a significant parameter that affects the conversion of FAME. The reaction was carried out by varying temperatures from 40 to 70 °C in which the conversion was increased from 40 to 94.5%. However, the reaction temperature was not increased beyond 70 °C due to the loss of methanol beyond its boiling temperature (Yan et al. 2008). Furthermore, at the boiling temperature, the greater amount of methanol is in a vapour state without in contact with the reaction mixture. Figure 8(c) shows the biodiesel conversion with respect to reaction temperature.

3.9.4 Reaction time

Figure 8(d) shows the outcome of reaction time on the conversion of biodiesel. The maximum conversion was attained at 120 min at 70°C, 6 wt % HAC loading, 400 rpm and 15:1 methanol to oil ratio. Further, an increase in reaction time did not increase the conversion because the reaction reached equilibrium. The previous work suggested the conversion of biodiesel depended on reaction time. It was depicted that incrementing the reaction time gives a better result until the optimum reaction time is reached (Mardhiah et al. 2017).

3.9.5 Stirring rate

The stirring rate significantly contributes to the sufficient contact between reactants and speeds up the reaction to attain a higher conversion. Figure 8(e) shows the stirring rate versus conversion at optimum conditions. The optimum stirring rate was 500 rpm with a maximum FAME conversion 98.5%. Further, an increase in stirring rate does not improve the conversion. This may be due to the enhancement of reversible reactions (Vivek and Guptha 2004).

3.10 HAC Stability and Reusability

The catalyst reusability reduces the process cost. After completion of each cycle, the HAC was strained using No. 1 Whatman filter paper, washed using petroleum ether and dried at 60 °C in a hot air oven for 5 h. The recycled HAC was used for each cycle and the reaction was performed at optimum conditions. The results are represented in Fig. 9. It can be observed that the HAC can be recycled six times with a conversion above 90%. The biodiesel produced from the oil having a conversion of above 90% will be in line with the ASTM standards. The conversion of biodiesel reduced below 90% from the seventh cycle due to the leaching of active sites and deposition of the products and reactants on the surface of the HAC (Sadba et al. 2015).

3.11 Biodiesel Characterisation

One step of HAC esterification and transesterification was performed to produce biodiesel. Figure 10 represents the FTIR spectra of *C. tabularis* oil and biodiesel. The biodiesel shows a broad peak at 3435 cm^{-1} indicating the bending and stretching of -OH vibrating due to water molecules. The presence of water in biodiesel and the absence of the same in oil may be due to the byproduct water produced during the esterification of FFA. The peaks formed at 2922 and 2854 cm^{-1} are found in both oil and biodiesel, representing the un-symmetric and symmetric stretching vibration of C-H in CH_2 and CH_3 groups. The conversion was confirmed by the characterised absorption peaks of methoxy-carbonyl and C = O stretching. The strong peak at 1740 and 1742 cm^{-1} is associated with C = O stretching vibration in the ester groups present in oil and biodiesel. The peak value of 1436 cm^{-1} corresponds to the presence of $-\text{CH}_3$ with the asymmetric bending vibration in methyl ester in the aliphatic chain (Booramurthy et al. 2020). The shifting of oil peaks from 1440 to 1436 cm^{-1} and from 1118 to 989 cm^{-1} clearly suggests the conversion of oil to biodiesel (Nisar et al. 2017).

The conversion of *C. tabularis* oil to FAME was determined using ^1H NMR. The 94% conversion of *C. tabularis* oil was produced under optimum conditions. The ^1H NMR spectroscopy accounted in Figs. 11(a) and 11(b) showed the optimum biodiesel conversion was 99.2%.

The physiochemical properties of biodiesel mainly depend on feedstock and production methods. Standard methods are used to determine the fuel properties of FAME and the results are compared with ASTM D6751 standard as listed in Table 8. The viscosity of the *C. tabularis* biodiesel was low, enhancing

the fuel flow in the engine pump and atomisation properties in the fuel injector. The high flash point of the fuel improves the storage stability and safe handling. The cetane index value of 48 represents improved ignition delay. Ca, Mg, Na, sulphate and acids are lower than the standard representing less corrosion and erosion in engine parts. The reduced value of carbon residue lowers engine corrosion and increases combustion efficiency. Water and sediments are under the limit, suggesting the fuel will be free from microbial contamination during prolonged storage. Since the fuel produced is within biodiesel standards, it can be used directly in combustion engines without or with slight modification. Moreover, the fuel can be blended with petroleum diesel at any proportion (Reham et al. 2015).

Table 8
Fuel properties of *C. tabularis* biodiesel

Properties	Unit	Test method	ASTM D6751 standard	<i>C. tabularis</i> biodiesel
Specific gravity	-	ASTM D4052	-	0.850
Flash point	°C	ASTM D93	130 min.	140
Cloud point	°C	ASTM D2500	Report	1
Viscosity @ 40 °C	mm ² s ⁻¹	ASTM D445	1.9-6.0	4.13
Acid number	mg KOH g ⁻¹	ASTM D664	0.05 max.	0.027
Carbon residue	% mass	ASTM D4530	0.05 max.	0.041
Water & sediments	% volume	ASTM D2709	0.05 max.	0.05
Copper strip corrosion	-	ASTM D130	Number 3 max.	1a
Sulphated ash	% mass	ASTM D874	0.02 max.	0.01
Phosphorous content	% mass	ASTM D4951	0.001 max.	0.0001
Na & K combined	ppm	EN 14538	5 max.	3.2
Ca & Mg combined	ppm	EN 14538	5 max.	3.1
Cetane index	-	ASTM D4737	47 min.	48
*min. is minimum; max. is maximum				

4 Conclusion

The oil extraction from AUH pretreated *C. tabularis* seed was done by the Soxhlet extraction method. The n-hexane was selected based on the maximum oil yield (32%). Further, the batch method was used to study the kinetic and thermodynamic properties of the extraction. The extraction data showed that it follows first order kinetics and their rate constants and thermodynamic parameters were calculated. The activation energy and Arrhenius constant are 63.604 kJ mol⁻¹ and 66.66x10⁴ s⁻¹, respectively. The extracted *C. tabularis* oil had high FFA; hence it was subjected to a one step esterification and transesterification reaction using HAC. The HAC was synthesised using a chemical reduction process and its physiochemical properties are also analysed. The process parameters influencing the biodiesel conversion were optimised. An optimum conversion of 99.2% was obtained at 6 wt% HAC loading, 15:1 methanol to oil molar ratio, 70 °C reaction temperature, 120 min reaction time and 500 rpm stirring rate. Further, the physiochemical characteristics of biodiesel were identified using standard methods and compared with ASTM D6751 standard.

Declarations

Ethical Approval

Not applicable.

Consent to Participate

Not applicable.

Consent to Publish

Not applicable.

Authors Contributions

Yuvanashree Eswaramoorthi: Conceptualization, Data curation, Visualization, Formal analysis, Investigation, Methodology, Resources and Writing original draft; **Sivakumar Pandian:** Data curation, Visualization, Writing original draft, Writing review and editing; **Renganathan Shadevan:** Supervision, Project administration, Writing original draft, Writing review and editing.

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Competing Interests

The authors declare no competing interests.

Availability of data and materials

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Figures

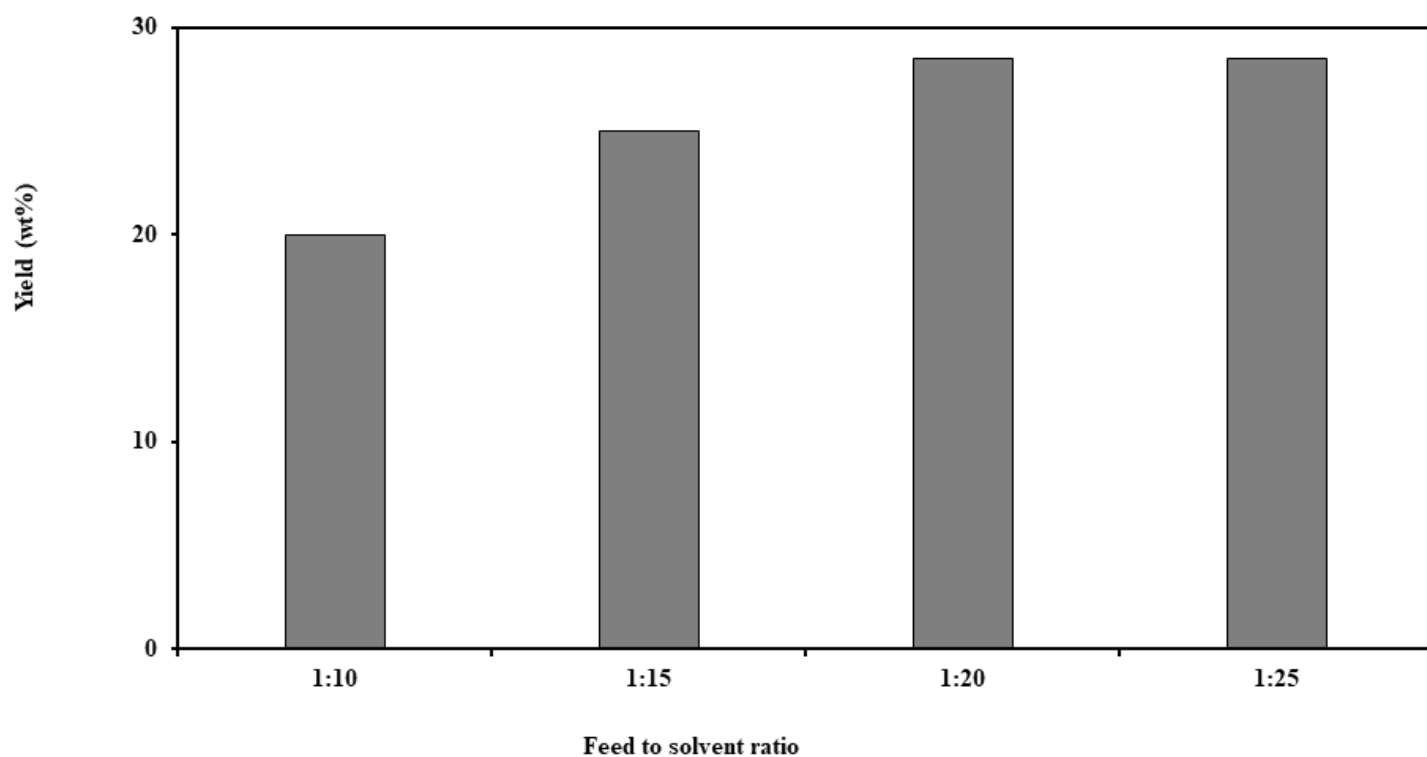


Figure 1

Feed to solvent weight ratio at 50 °C and 90 min

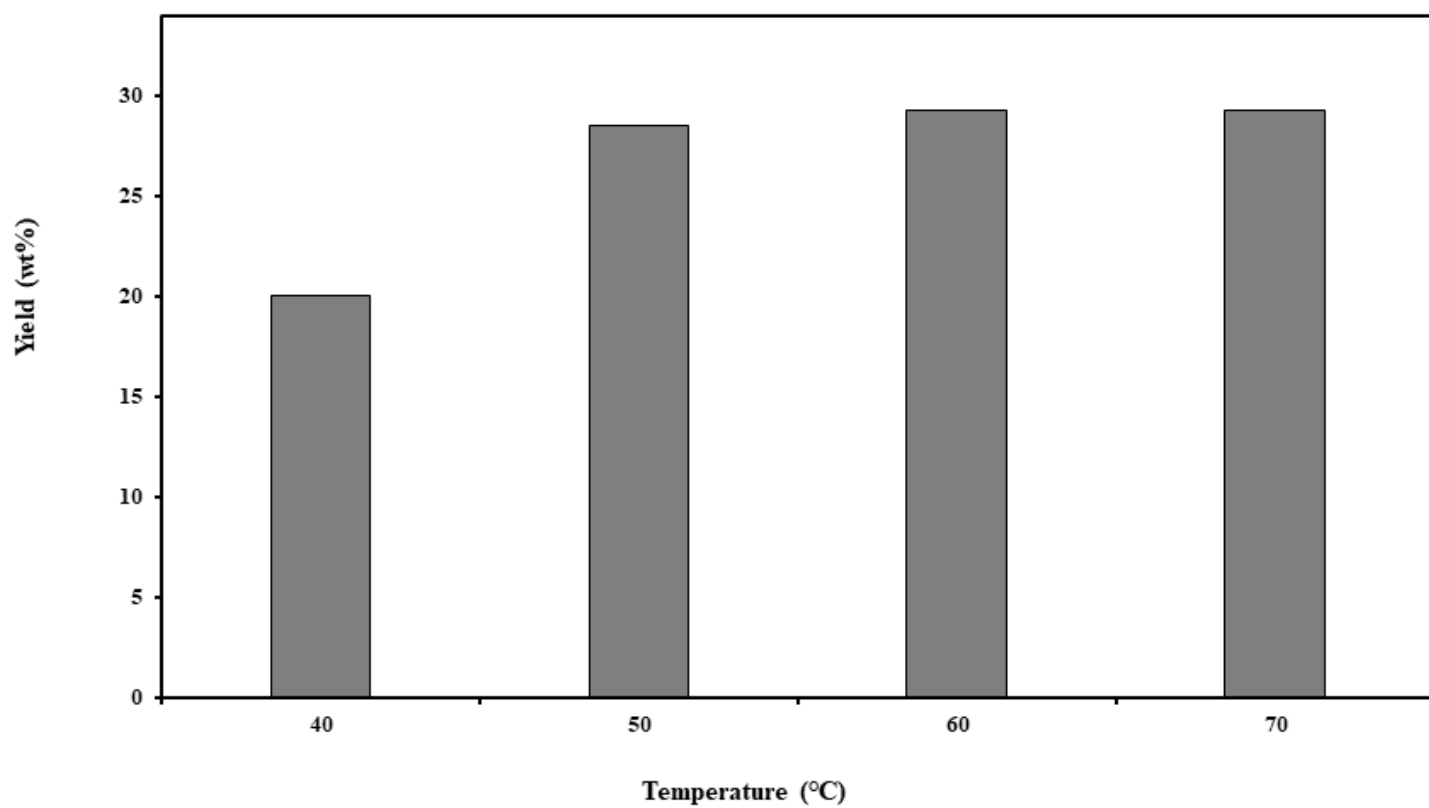


Figure 2

Effect of temperature at 1:20 feed to solvent ratio and 90 min

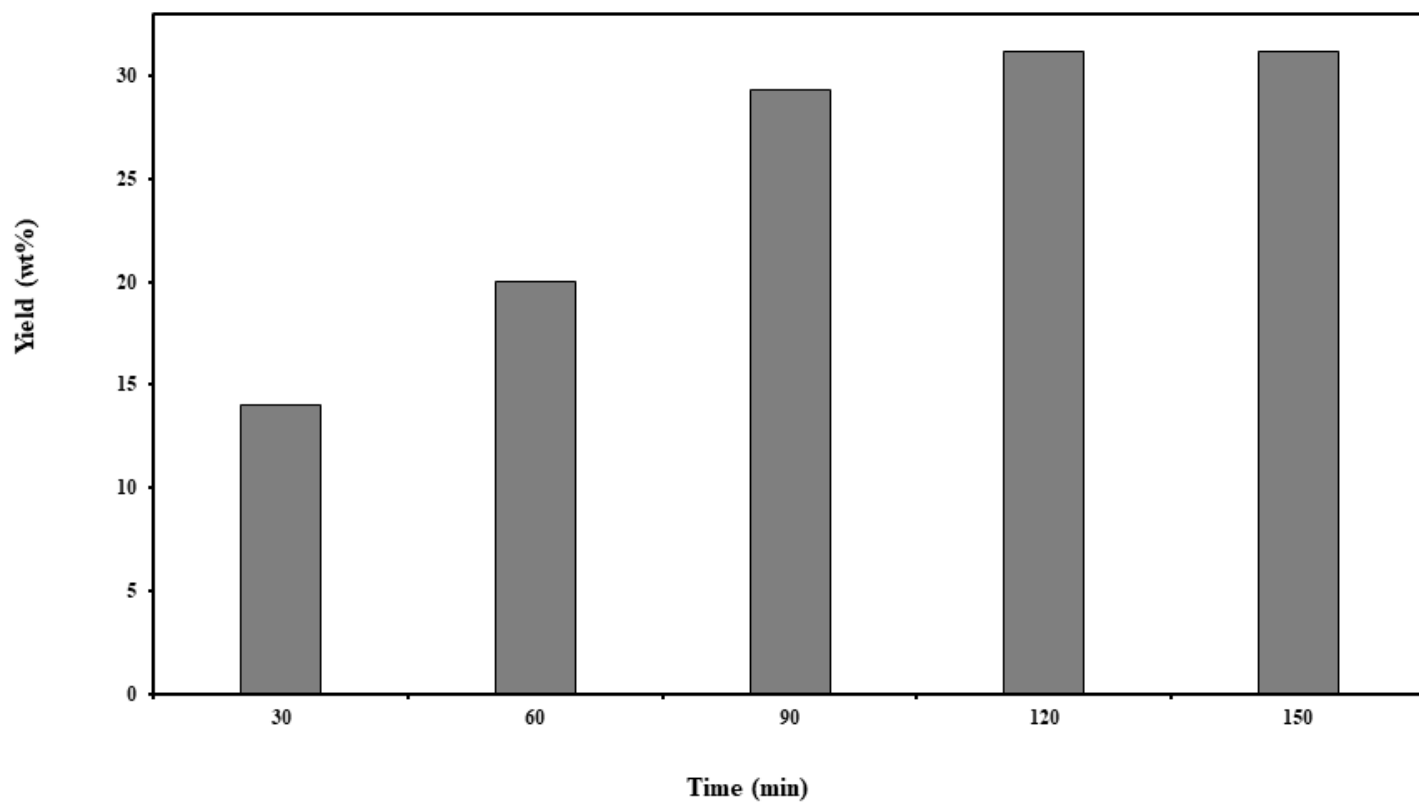


Figure 3

Effect of extraction time at 1:20 feed to solvent ratio and 60 °C

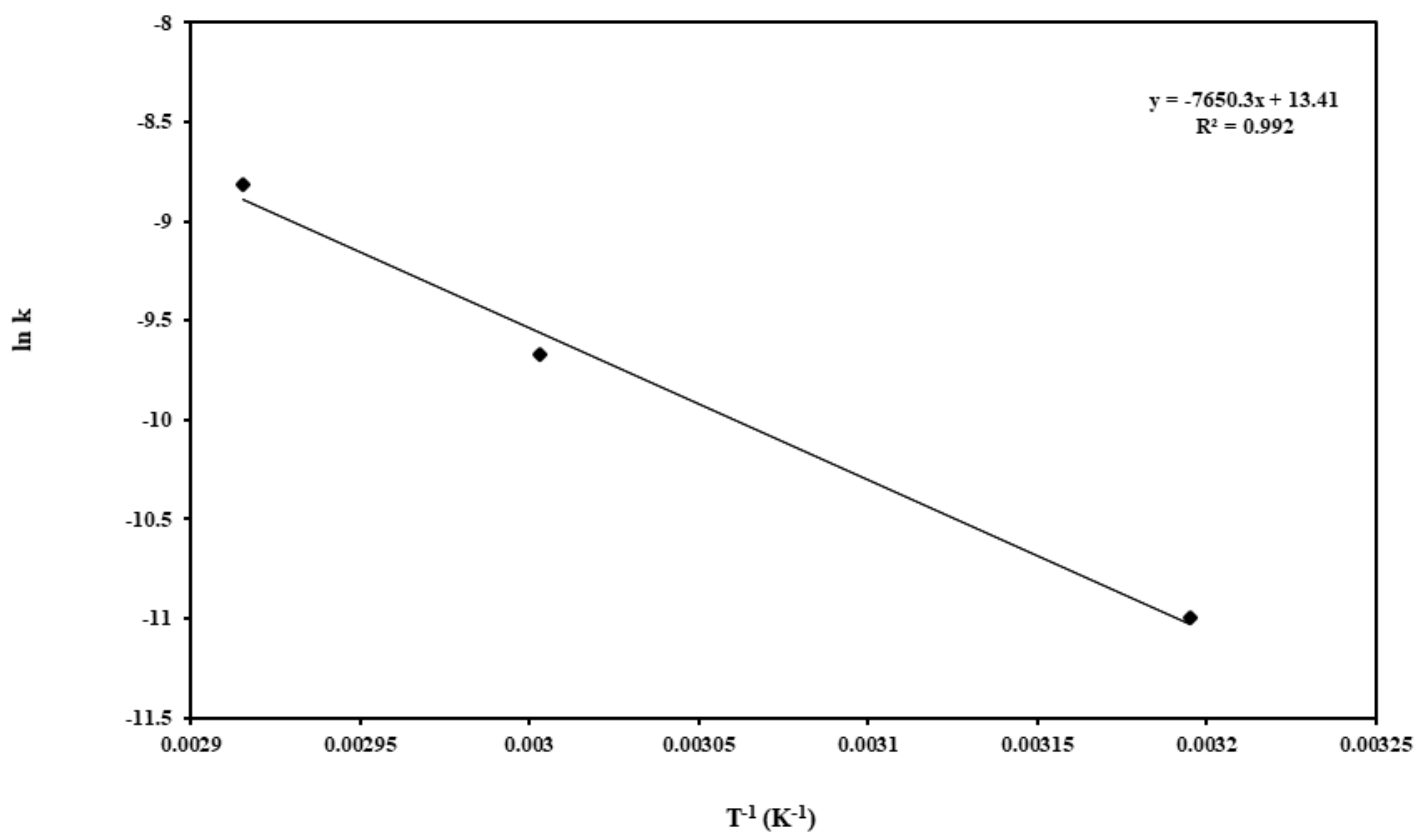


Figure 4

The plot of $\ln k$ vs. T^{-1}

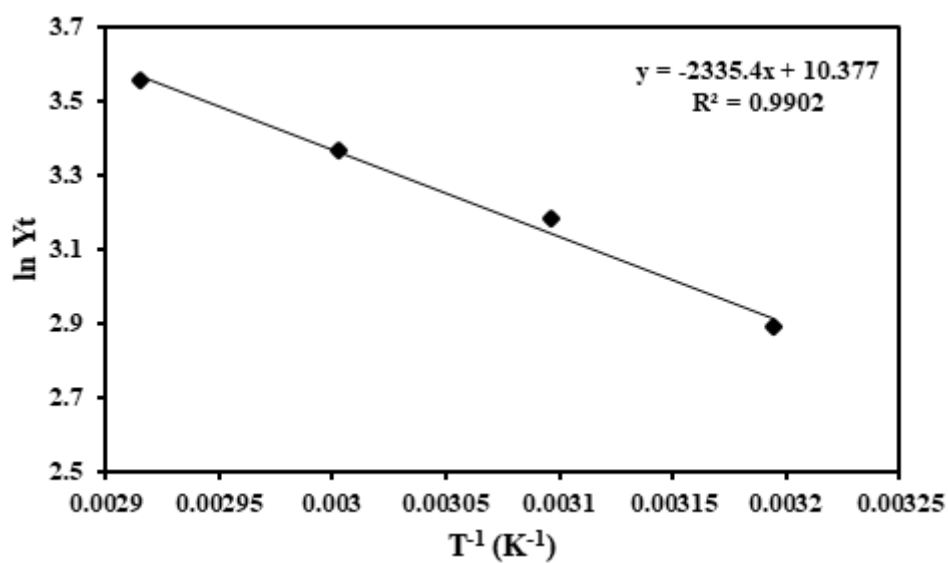


Figure 5

The plot of $\ln Y_t$ vs. T^{-1} at 120 min

Figure 6

- (a). SEM image of catalyst precursor
- (b). SEM image of HAC

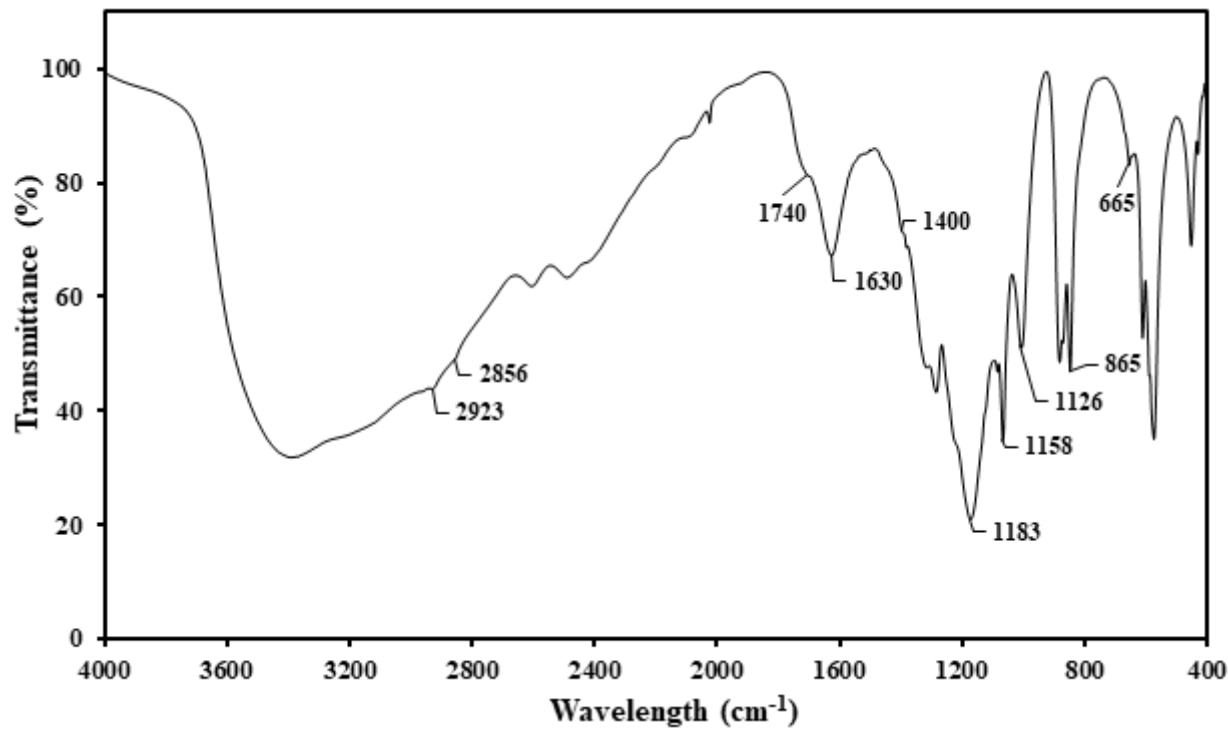


Figure 7

FTIR spectra of HAC

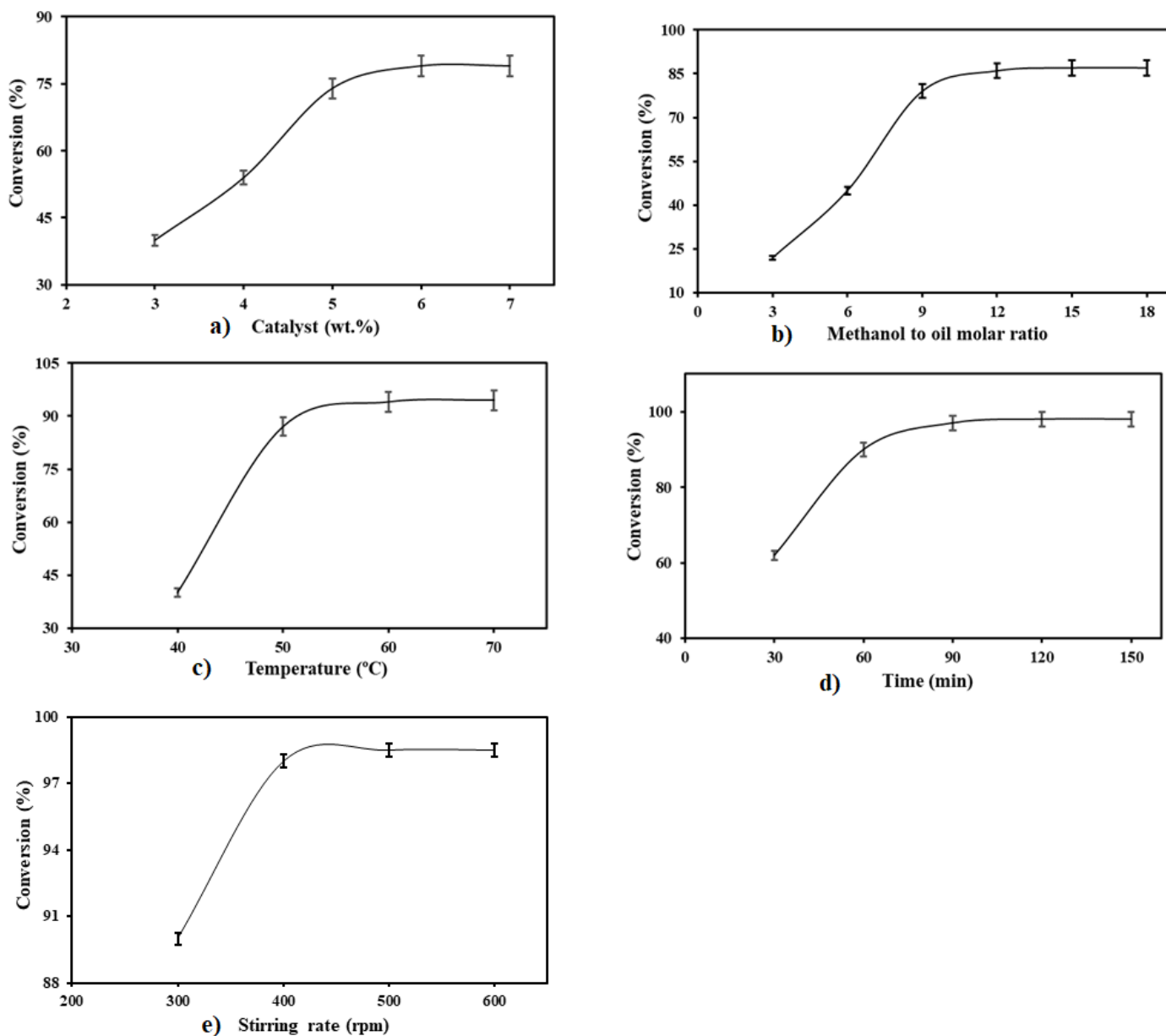


Figure 8

(a). Effect of HAC loading at 9:1 methanol to oil molar ratio, 50 °C reaction temperature, 60 min reaction time and 400 rpm stirring rate

(b). Effect of methanol to oil molar ratio at 6 wt% HAC loading, 50 °C reaction temperature, 60 min reaction time and 400 rpm stirrer speed

(c). Effect of reaction temperature at 15:1 methanol to oil molar concentration ratio, 6 wt% HAC loading, 60 min of reaction time and 400 rpm stirring rate

(d). Effect of reaction time at 6 wt % HAC loading, 15:1 methanol to oil molar ratio, 70 °C reaction temperature and 400 rpm stirring rate

(e). Effect of stirring speed at 6 wt % HAC loading, 15:1 methanol to oil molar ratio, 70 °C reaction temperature and 60 min of reaction time

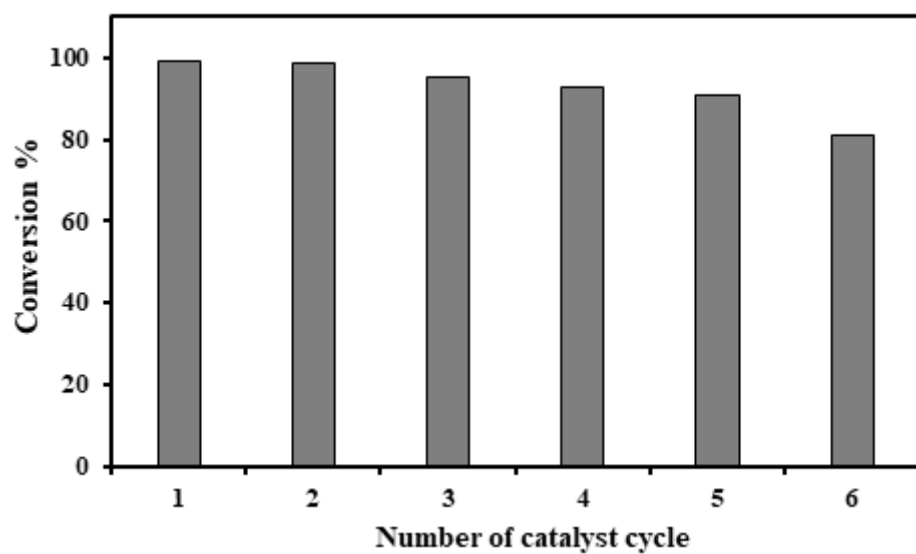


Figure 9

Number of HAC cycles versus conversion of FAME

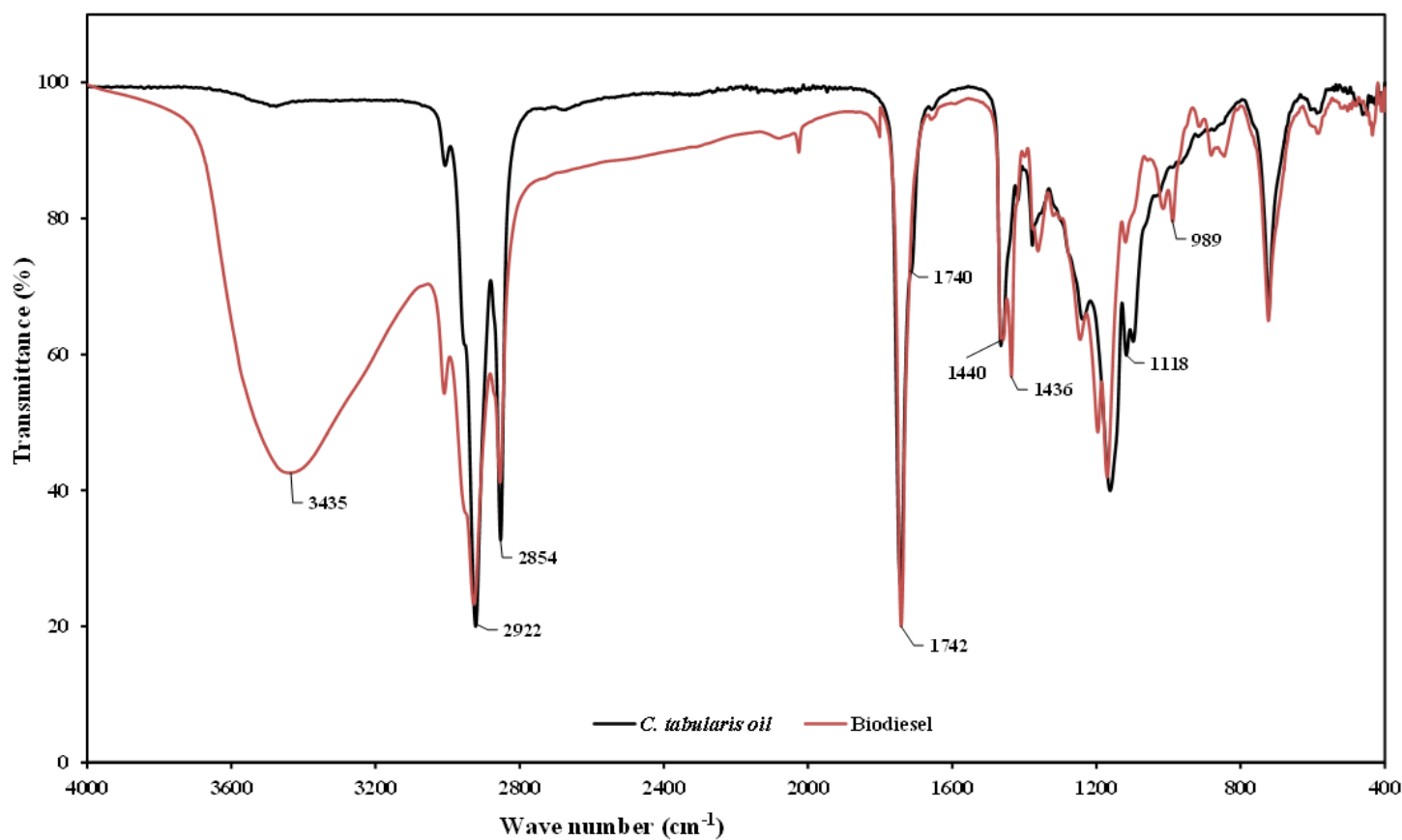


Figure 10

FTIR spectra of *C. tabularis* oil and biodiesel

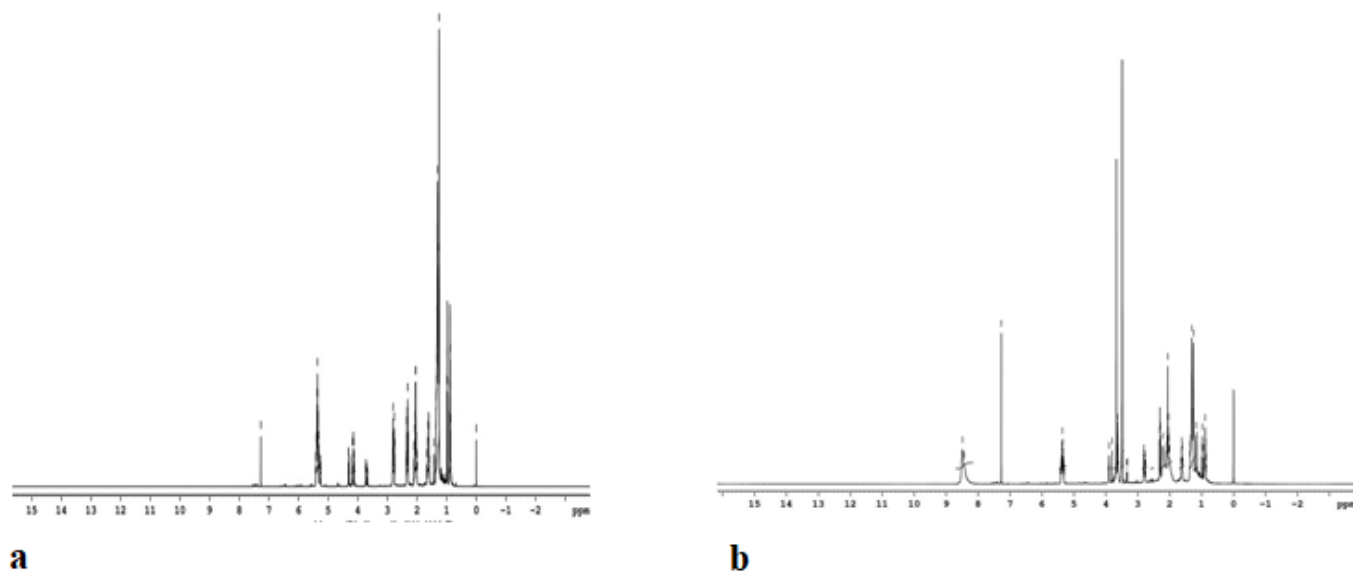


Figure 11

(a). ^1H NMR spectra for *C. tabularis* oil

(b). ^1H NMR spectra of 99.2 % conversion of *C. tabularis* oil under optimum condition