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BIODIESEL PRODUCTION FROM WASTE ANIMAL FAT USING A NOVEL CATALYST HCA IMMOBILIZED AuNPS AMINE GRAFTED SBA-15

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Abstract

The fleshings produced during the pre-tanning process in tanneries and animal wastes generated from slaughterhouse are causing serious environmental concern because of improper disposal techniques. The fats extracted from these wastes were used as feedstock for the production of biodiesel, which serves as an alternate for conventional diesel fuel because of their sustainability. The use of these animal fats ruled out the issues over the "food vs. fuel" conflict, as edible feedstocks were used in the production of biodiesel earlier. This work deals with the production of biodiesel from waste animal fats by the means of methanol-based transesterification using nanoparticles as a heterogeneous catalyst. A maximum fat recovery of 85% was achieved by the means of autoclave heat treatment method. The refining of fat was carried out through acid degumming, where orthophosphoric acid was mixed with the fat to remove the phospholipids as residues. Pretreatment of the extracted fat was done using glycerolysis, where the FFA % of these fats was reduced from 7% to 0.25% with a recorded efficiency of 96.4%. N catalyzed transesterification was carried out by investigating various operating parameters like oil/alcohol molar ratio, catalyst concentration, temperature and reaction time and optimizing them. The optimized process parameters produced a maximum yield of 94% biodiesel. The synthesized novel catalyst - HCA immobilized AuNPS AMINE grafted SBA-15 was characterized using spectral data. Besides, the residual glycerol is defined as a value-added product to meet its application in the glycerolysis process as a reactant.

Keywords: Animal fat, Fleshing wastes, Glycerol, Glycerolysis, Slaughterhouse wastes, Transesterification.

1. Introduction

Energy is the physical resources that constitute as a primary requirement for the human beings. Increase in demand for energy has grown rapidly over decades due to modernization and population growth. An effective solution for the energy demand can be addressed by renewable energy resources. Numerous researches have been carried out for studying these alternate energy resources for effective utilization and management [1]. Biodiesel is one such renewable biofuel, which is produced by transesterifying triglycerides, in vegetable oil or animal fats, with alcohol catalyzed by either a homogeneous catalyst or heterogeneous catalyst.

Most commonly used alcohols are methanol and ethanol whereas the catalyst can be acidic (sulphuric acid) or basic (sodium hydroxide, potassium hydroxide) or enzymatic. Biodiesel possesses unique properties like high cetane number, high oxygen content [2-4] with no aromatics and zero sulphur content [5, 6] and as carbon-neutral fuel, which makes it suitable for combustion based applications. Also, the biodiesel is known for its reduced emissions where it produces the very low level of CO, NO_2, hydrocarbons, Polycyclic Aromatic Hydrocarbons (PAH), nitric Polycyclic Hydrocarbons (nPAH) and also particulate matter [3, 7, 8]. Apart from its environmental factors, this biofuel is known for its social and economic factors in many developing countries [9].

Generally, feedstocks for biodiesel must have good triglyceride content, easily available at low cost [10] and must obey "food vs. fuel" conflict. Waste animal fat can be considered as no-cost high potential feedstock for biodiesel production that follows the principles of "waste to energy" technique. These fats can be directly used as a fuel for the engine as emulsions with petrol-fuels, but because of its high viscosity, they are not ready to be used as fuel [11, 12]. Various studies have been conducted on animal fat as feedstock for biodiesel production. The feasibility of the biodiesel production from animal fat was studied by transesterifying the waste fleshing oil and evaluating its performance on a diesel engine [13].

As the feasibility of production was studied, the physical and chemical properties including the combustion and emission characteristics were identified for biodiesel produced from chicken and mutton wastes [14]. Duck tallow was transesterified using potassium hydroxide as catalyst, produced a yield of 97%. This work also concluded that the biodiesel formed was an oleate-based ester. [15]. Fleshing wastes, rich in fat content, can also be considered as an alternative feedstock for production of biodiesel, which can be blended with ordinary diesel [16, 17].

The sources for these animal fats are usually from leather industries and animal slaughterhouses in form of discarded wastes. Mostly as solid waste of about 55%, these animal fats are produced during pre-tanning stages of leather production like trimming, prefleshing, fleshing and shaving [18] whereas, in slaughterhouses, they can be obtained during butchering and meat processing process. In this work, the biodiesel is produced from animal fat extracted from leather fleshing and animal slaughterhouse wastes, by pretreating it with glycerolysis to reduce its initial FFA content followed by alcohol-based transesterification catalyzed by HCA Immobilized AuNPS amine grafted SBA-15 by optimizing various reaction parameters.

2. Materials and Methodology

2.1. Collection of samples

The raw fleshing wastes were collected from Central Leather Research Institute (CLRI) tannery section whereas the slaughterhouse wastes were collected from in and around Adyar, Chennai. These samples were preserved before they were subjected for further processes.

2.2. Extraction of fat

The collected samples were soaked in the water for 12 hours before it was neutralized with boric acid in order to reduce the pH concentration from 10 to 7. After neutralization, the animal wastes were autoclaved at 15 bar and 120 ^{o}C. This made the fat to be separated from other non-fatty residues and float on top. These fats were then collected and heated at 60 ^{o}C to remove the residues carried along with the fat.

2.3. Degumming of fat

The phospholipids existing in the fat were removed by the means of degumming. In this process, the orthophosphoric acid of 1% of oil content was stirred with fat for 10 minutes at 250 rpm and subjected for prolonged heating for another 10 minutes. The phospholipids were settled at the bottom as lecithin in form of dark brown residue.

2.4. Glycerolysis of fat

The concentration of Free Fatty Acids (FFA) was identified by the means of FFA titration. The reduction in FFA% was achieved by the means of glycerolysis reaction. The fat was mixed with glycerol in varying mixing ratios between 1:1 and 1:3, for various reaction temperatures and time with constant stirring speed. After the completion of the reaction, the glycerol dissolved with water settled down at the bottom while the fat was at the top.

2.5. HCA Immobilized AuNPS AMINE grafted SBA-15

A 50 mM of CPTMS was added to 1 g of SBA-15 dispersed in 70 ml of dry toluene under vigorous stirring. Then the mixture was refluxed at 80 °C for 24 h and the final product was filtered, washed with toluene followed by alcohol and dried under vacuum at 70°C for 8 h. The product was denoted as CPTMS/SBA-15. 1 mmol of amine compounds (TAEA/OAPS) was subsequently grafted on 1 g CPTMS/SBA-15 by procedure adopted for CPTMS grafting, while OAPS grafting was done in THF. The products were named as TAEA/SBA-15 and OAPS/SBA-15. 100 mg of TAEA/SBA-15 and OAPS/SBA-15was dispersed in 10 ml of 0.1 mmol tetrachloroauric acids ($HAuCl_4$) was added, the mixture was stirred at room temperature for 4 h. Then, controlled reduction of $HAuCl_4$ was done by dropwise addition of Sodium borohydride ($NaBH_4$) solution and continued stirring for another 24 h. Finally, the solid product was filtered, washed, dried under vacuum at 70 °C. The products are denoted as Au/TAEA/SBA-15 and Au/OAPS/SBA-15.

2.6. Transesterification of fat

The pretreated fat was subjected for transesterification reaction using the novel catalyst. The reaction was optimized by varying the molar ratio between 1:1 to 1:6, for various catalyst concentrations from 0.1 to 2.0%, for various operating temperatures between 50 ^{o}C and 70 ^{o}C. The reaction mixture was then subjected for separation using separating funnel.

2.7. Refining of biodiesel

After separation, the layer at the top was biodiesel whereas the layer at the bottom was glycerol. The separated biodiesel was initially cleaned with the residual glycerol obtained as the by-product of glycerolysis by stirring it with 20 minutes to remove any residual glycerol present in it. After glycerol treatment, the refined biodiesel was water washed at 60 ^{o}C for 15 minutes. After washing, the mixture was allowed to settle down for 24 hours where the refined biodiesel was obtained. The refined biodiesel was heated for 110 ^{o}C to remove any water content from it.

2.8. Refining of glycerol

The glycerol obtained as the byproduct of transesterification reaction was taken along with the glycerol resulted as a residue after the refining of biodiesel, was acidified by adding 31.45% of hydrochloric acid to reduce the pH below 1. After removing the impurities, the glycerol was neutralized with sodium hydroxide and was heated at 110 ^{o}C to remove moisture content. The heated glycerol was mixed with 4 times its quantity of methanol to decolourize it. Finally, the methanol was removed from the glycerol by means of distillation leaving behind pure glycerol.

3. Results and Discussions

The fat content in the leather fleshing and animal slaughterhouse wastes were determined by the soxhlet apparatus. This solvent extraction test revealed that the fleshing and slaughterhouse wastes had 8% and 20% of fat content from its wet weight respectively. The autoclave was used for the large-scale extraction of fat, which was used as feedstock in the biodiesel production. The maximum amount of fat recovery recorded using this method was 85%.

The presence of fatty acids was confirmed by the peaks obtained from the corresponding functional group. Figure 1 represents the FTIR spectra of the animal fat extracted from leather fleshing and animal slaughterhouse wastes. The peak with the intensity of 70.7406 corresponding to a wavelength of 1744.3 cm^{-1} explains about the presence of carboxyl group, which gives the evidence about the presence of fatty acids.

The mean molecular weight of the animal fat was found to be 860 kg/kg-mol. The Free Fatty Acid (FFA) content in the fat was found to be 7% during the time of extraction, which increases on prolonged exposure to the environment. The presence of moisture content in the environment causes the hydrolysis of fat, which leads to the formation of free fatty acid and glycerol. Higher concentration of FFA content in fat leads to the poor yield of biodiesel and favours saponification reaction. Glycerolysis reaction was carried out as a pretreatment method to convert Free Fatty Acids into fatty acids attached in glyceride spine. The reaction was carried out for a mixing ratio of 2.15 g/g glycerol to fat, the reaction time of 60 minutes and 110 ^{o}C as

reaction temperature, which was optimized using response surface method (RSM) software. The maximum efficiency recorded using this optimized method was found to be 96.4 %, which reduced the FFA% from 7% to 0.25%. Even though the required mixing ratio for glycerolysis was calculated as 2 g/g glycerol to fat, an excess of 7.5% of glycerol was added to avoid the backward reaction under equilibrium condition [19]. Figures 2(a), (b) and (c) illustrate the response surface curve of the optimized glycerolysis reaction for various parameters.

XRD patterns of SBA-15, Au/TAEA/SBA-15 and Au/OAPS/SBA-15 are shown in Fig. 3. The low angle XRD patterns of Au/TAEA/SBA-15 and Au/OAPS/SBA-15 show peaks at 2θ=0.8, 1.5 and 1.8, which reveals the presence of (1 0 0), (1 1 0) and (2 0 0) planes due to the well-ordered hexagonal mesophase. The intensity of these patterns appears to be less than the parent SBA-15, which is due to the pore filling by CPTMS grafting followed by TAEA/OAPS and immobilization of Au nanoparticles. The wide-angle XRD patterns of Au/TAEA/SBA-15 and Au/OAPS/SBA-15 confirmed the presence of gold (Au) nanoparticles at 2θ=38, 44, 65, 44.1, and 78°, corresponding to the faces (1 1 1), (2 0 0), (2 2 0) and (3 1 1), respectively (Fig. 3). The generated XRD pattern was similar to that of Gold Nanoparticles synthesized from aqueous root extract of Morinda Citrifolia L. [20].

The textural properties of SBA-15, Au/TAEA/SBA-15 and Au/OAPS/SBA-15 were obtained from N_2 adsorption-desorption isotherms; the results are summarized in Table 1. The surface area of the materials was evaluated using the BET method, the pore size by BJH method (isotherms with hysteresis). The nitrogen adsorption/desorption isotherms of all the materials exhibit type IV isotherm (figures not shown) with a well-defined hysteresis loop between partial pressures, P/Po=0.68-0.75, indicating mesophase. Obviously, for Au/TAEA/SBA-15 and Au/OAPS/SBA-15 there observed a decrease in the specific areas pore volume and pore diameter compared to SBA-15. Such significant decrease of textural properties of those materials is due to pore filling and/or structural construction of CPTMS and TAEA/OAPS followed by Au nanoparticles, which is in line with the XRD results.

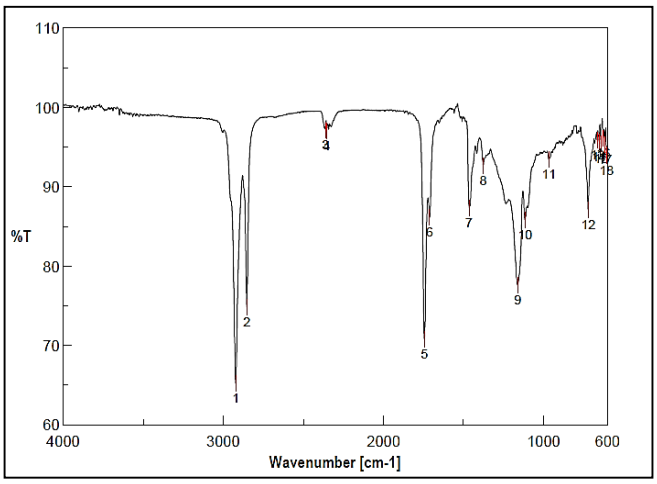
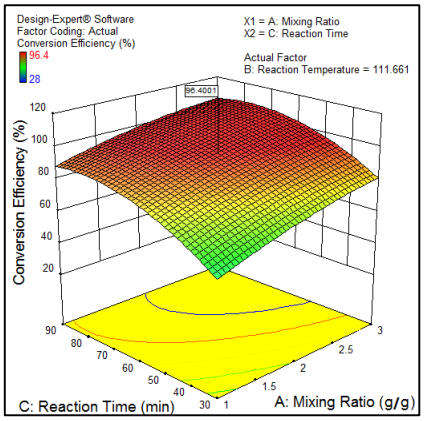
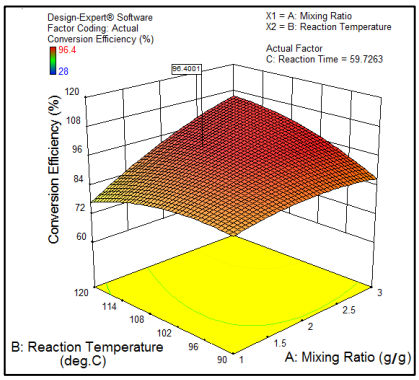


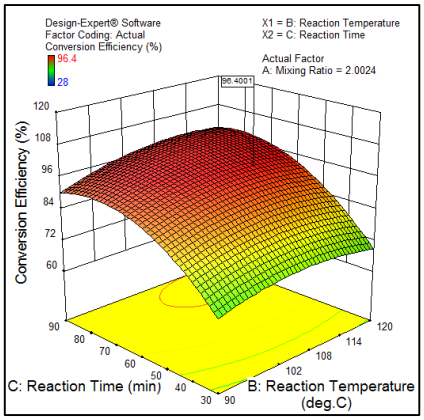
Fig. 1. FTIR peaks of waste animal fat.



(a). Surface plot between mixing ratio vs. reaction time (at actual reaction temperature).



(b) Surface plot between mixing ratio vs. reaction temperature (at actual reaction time)



(c) Surface plot between reaction temperature ratio vs. reaction time (at actual mixing ratio).

Fig. 2. Surface plot for various parameters of optimized glycerolysis reaction

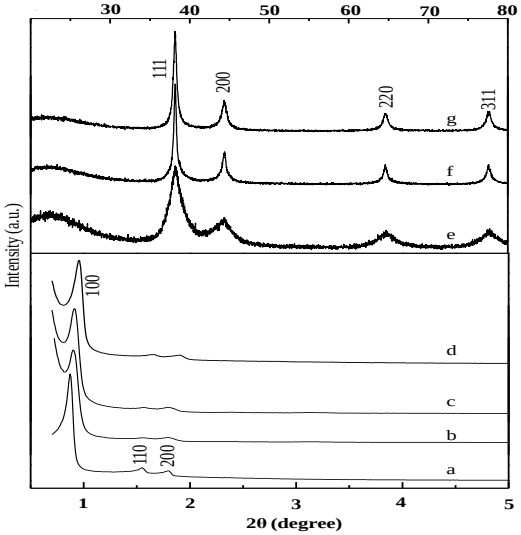


Fig. 3. XRD patterns of SBA-15(*a*), Au/TREN/SBA-15(*b, e*), Au/TEPA /SBA-15(*c, f*) and Au/OAPS/SBA-15 (*d, g*).

Table 1. Textural properties and zeta potential of SBA-15, Au/TAEA/SBA-15 and Au/OAPS/SBA-15.

Sample	S_{BET} (m^2/g)	V_p (cm^3/g)	D_p (Nm)	Zeta potential (mV)
SBA-15	633	1.42	15.2	-15.8
Au/TAEA/SBA-15	195	0.75	6.73	-8.23
Au/OAPS/SBA-15	138	0.56	5.87	-19.60

*****S_{BET}*surface area;* V_p*-mean pore volume* D_p*-pore diameter*.

The transesterification reaction was carried out by optimizing the parameters as follows: fat to methanol (molar ratio): 1:3, catalyst concentration: 0.5%, reaction temperature: 60 °C, reaction time: 60 minutes, stirring speed: 350 rpm. The optimized process parameters produced a maximum yield of 94% biodiesel, which was similar to that of biodiesel yield that was produced by transesterifying waste animal fat by means of acid catalyzed transesterification [21]. 93% yield of biodiesel was obtained when waste tallow was transesterified using $CaMnO_x$, CaO as a heterogeneous catalyst [22]. Improvised heterogeneous catalyst Mesoporous Silica diphenyl ammonium triflate yielded biodiesel of 96% when brown grease was transesterified [23]. This work proved that the synthesized catalyst functioned effectively in producing biodiesel from waste animal fat.

Figure 4 shows the effect of molar ratio on yield the yield of biodiesel. Generally, 1 mol of fat requires 3 mols of alcohol to produce 3 mols biodiesel and 1 mol of glycerol stoichiometrically. The reaction was carried out keeping the catalyst concentration as 0.5% constantly and varying the molar ratio from 1:1 to 1:6 the operating parameters were maintained at 60 °C, 350 rpm, and 60 minutes. Methanol was used as the solvent for carrying out the transesterification reaction. As the molar ratio increased from 1:1 to 1:3, the yield increased from 70% to 94 %. This was because of attainment of stoichiometric ratio in the reaction, which

tends to produce the most productive yield. As the molar ratio was increased from 1:3 to 1:6, the yield of the FAME drastically reduced from 94% to 82%. The reduction in yield was due to the low availability of alcohol for the reaction to proceed in the forward direction.

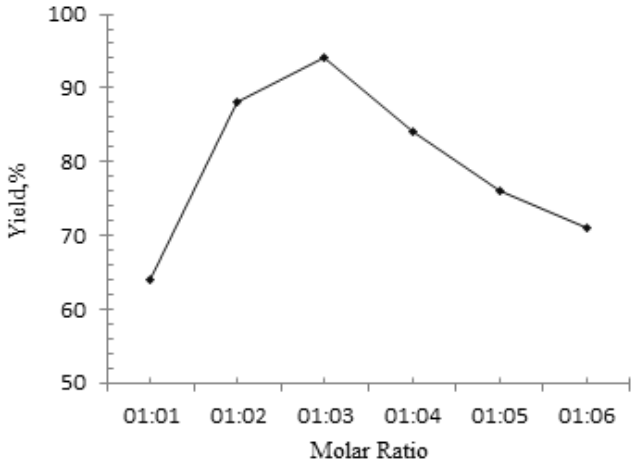


Fig. 4. Effect of molar ratio on yield.

Figure 5 represents the effect of a catalyst on yield. The reaction was carried out keeping the molar ratio as 1:3 constantly and varying the catalyst concentration from 0.1% to 2%.the operating parameters were maintained as 60 ^{o}C, 350 rpm, and 60 minutes. It was clearly proven that HCA Immobilized AuNPS AMINE grafted SBA-15 was a very effective catalyst among the other base catalysts and also among the other acid and enzymatic catalysts. The graph inferred that catalyst concentration below 2% favoured transesterification whereas more than that resulted in a decrease in the yield. The most optimized catalyst concentration was found effective at 0.5% because of the low acid value of the fat, which was achieved after the pretreatment.

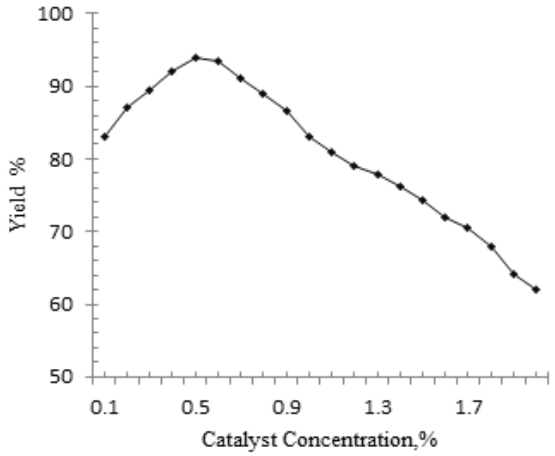


Fig. 5. Effect of catalyst concentration on yield.

The temperature for the transesterification reaction was optimized by keeping the parameters like catalyst concentration and molar ratio constant and varying the temperature from 50 to 70 °C. From Fig. 6, it can be noted that the most optimum temperature for transesterification was found to be 60 °C which has been producing very effective yield compared to other temperatures. At 60 °C temperature, the animal fat was completely in liquid form and the bond between the fats experienced a weak Van der Waal's force of attraction and was ready to attract any strong nucleophilic substance that was present in the reaction mixture. Simultaneously, the methanol in the liquid-vapour phase was hyperactive and this readily combines with the fats thus favouring the transesterification reaction accompanied with good conversion rate.

The synthesized biodiesel was analysed using the FTIR where the peak with a wavelength of 1742.37 cm^{-1} for an intensity of 64.0286 confirmed the presence of an ester group. Figure 7 represents the FTIR spectra of biodiesel produced from waste animal fat.

The quantification of fatty acids was carried out using GC-MS, which identified the palmitic and oleic acids as the dominant fatty acids present in the fat. Figure 8 shows the GC-MS spectra of the biodiesel produced from waste animal fat.

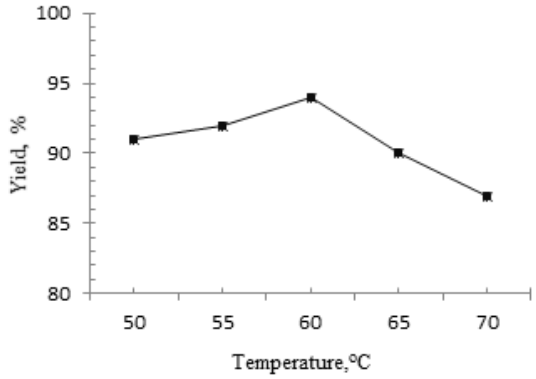


Fig. 6. Effect of temperature on biodiesel yield.

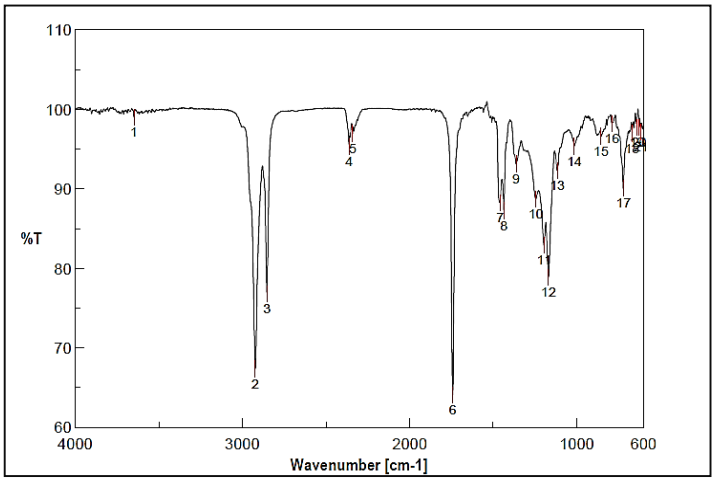


Fig. 7. FTIR spectra of waste animal fat biodiesel.

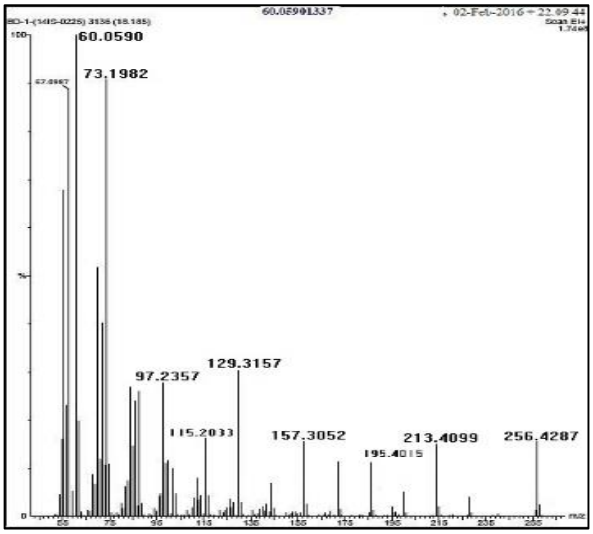


Fig. 8. GC-MS spectra of waste animal fat.

4. Conclusion

The maximum yield of biodiesel from animal fat was achieved by regulating various parameters like molar ratio, amount of HCA Immobilized AuNPS AMINE grafted SBA-15 catalyst added, reaction time, methodology involved and temperature conditions. The synthesis of biodiesel initiated with the extraction of fat followed by the pretreatment of the fats by the mean of glycerolysis reaction. Glycerolysis was carried out by adding oil to glycerol in a ratio of 2.5 g/g of oil at 110 ^{o}C for 90 minutes. The biodiesel was synthesized by means of using transesterification on animal fat for a molar ratio of 1:3 with a catalyst concentration of 0.5%, at 60 ^{o}C, 350 rpm for 60 minutes. The FTIR and GC-MS spectrophotometry spectra confirmed the presence of fatty acids in animal fat and also proved the conversion into Fatty Acid Methyl Ester. A 94 % of yield was achieved from this process and various physiochemical properties and performance-based analysis will be done for characterizing and improvising the bio-diesel for further works.

Abbreviations

AuNPs	Gold Nanoparticles
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
CPTMS	Chitosan (CTS)/(3-Chloropropyl) Trimethoxysilane
FAME	Fatty Acid Methyl Ester
FFA	Free Fatty Acids
FTIR	Fourier Transform Infrared Spectroscopy
GC-MS	Gas Chromatography-Mass Spectrometry
HCA	Human Carbonic Anhydrase
OAPs	Octahedral Anatase Particles
SBA	Mesoporous Silica
TAEA	Tris (2-Aminoethyl) Amine
XRD	X-ray Diffraction

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