

Upgrading Sawdust (*Vitellaria paradoxa*) Pyrolysis Oil using locally Developed Catalyst from Poultry Eggshell

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Abstract

In this research work, sawdust (*Vitellaria paradoxa*) was thermo-chemically converted with and without catalyst (CaO) formulated from poultry eggshell to demonstrate its upgrading potential towards producing fuels and chemicals. Physicochemical characterization of the biomass confirmed its bioenergy potential for producing renewable fuel. Thermal pyrolysis of the biomass was performed at 300°C and 500°C at 10°C/min heating rate, and 100 mL/min nitrogen flow rate, whereas catalytic pyrolysis was performed with CaO at 10 (wt%) catalyst loading. The highest pyrolytic liquid yield by thermal pyrolysis was found to be 8.60 (wt%) for 300 °C, and increased to 13.0 (wt%) at pyrolytic temperature of 500°C. Results indicated insignificant decreasing liquid yield by just 0.30 (wt%) for 300°C and by – 0.04 (wt%) for 500°C respectively. Products characterization by FTIR analysis showed prominent selectivity towards aromatic, phenols, alkanes, alcohols, acids and aldehydes as major components. Also, GCMS analysis confirmed that use of catalyst reduced the content of oxygenated and acidic compounds and increased that the amount of alcohols and aldehydes. It is concluded that, catalytic pyrolysis of sawdust using synthesized eggshell selectively produced energy-rich products and reduced oxygenated compounds.

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1. Introduction

Biofuel is one of the promising options of renewable energy gaining popularity globally, as it can produce fuel with similar functionality of crude oil [1]. In these fuels production, organic waste or biomass is subjected to degrade by means of micro-organism or thermal decomposition to produce liquid and gaseous fuel using different conversion techniques. Thermochemical conversions include combustion, gasification, pyrolysis, and hydrothermal liquefaction. Pyrolysis is the process used to provide solid, gas, and liquid type of fuels, as per the need. Pyrolysis oil or Bio-oil produced from the pyrolysis of biomass has been identified as potential fuel to replace fossil fuel in many applications, if produced and processed properly [2]. Presently, fast pyrolysis and hydro-thermal liquefaction are the two most used techniques for bio-oil productions. The fast pyrolysis of biomass required the following conditions, the higher heating rate for rapid thermal decomposition of biomass i.e., $> 100\text{ }^{\circ}\text{C}/\text{min}$, size of biomass $< 1\text{ mm}$, and controlled temperature of 500°C [3]. The bio-oil has ten times more density than the raw or loose biomass, it is easy to transport and can be used as an efficient energy carrier. Bio-oil has higher heating value between 16–19 MJ/kg. Despite the above advantages, bio-oil has limitations such as high water content, high viscosity, and low heating value [4]. The presence of organic acids causes corrosion to common materials as well as aldehydes and large molecular oligomers make it difficult to use bio-oil as transport fuel [5]. Therefore, to replace partially or fully transportation fuel by bio-oil, it is necessary to improve the quality of bio-oil by upgrading. A number of research papers had reported varying composition of pyrolysis oil. According to Haarlemmer et al., [6], the bio-oil produced from beech wood via hydrothermal and fast pyrolysis exhibit distinguishing properties such as in its acidity, iodine value and carbon residue content, high viscosity and low volatility, suggesting the properties of the products are not necessarily feedstock dependent but also process dependent as well. On the contrary, the yields distribution during pyrolysis of lignin also depends on the composition of the feedstock. Chang et al. [7], conducted a Py-GC/MS degradation of palm kernel shell, reporting the primary composition of the feedstock indicated the predominance of p-hydroxyphenyl structural units, resulting in high phenolic products, often its degradation. In contrast, pine sawdust and wheat straw contained largely guaiacyl units, and often degradation, yielded significant proportion of methoxy groups. Similarly, Biswas et al. [8], reported the slow pyrolysis of prot, alkali and dealkaline lignin for the production of chemicals. Among these types, alkali lignin was reported to have highest bio-oil yield (34.1 wt%). Bio-oil products showed the presence of guaiacol, syringol, alkylphenols and catechol; depending on the pyrolysis conditions and nature of lignin used. Pyrolysis of lignin-rich biomass from cotton by-product was conducted by Chen et al., [9]. Maximum bio-crude oil yield from fast pyrolysis was 58.13 (wt%) and 45.01 (wt%) at $600\text{ }^{\circ}\text{C}$ for cotton exocarp and spent mushroom substrate of cotton by-products, respectively. Products of co-pyrolysis have wide range of applications. The bio-char from the co-pyrolysis of biomass and tyre was found to be predominantly mesoporous in nature and increases the oxygen functionality as well as the surface area due to the waste tyres. Consequently, the mineral composition of produced char was improved and was effective in lead sorption, which was accompanied by a significant release of Ca^{2+} and Zn^{2+} as proven by the kinetics studies conducted by Barnardo et al., [10]. The choice of technology for pyrolysis largely depends on the process economics and the desired products of interest. For example, the use of thermal plasma as an energy source for pyrolysis/gasification showed the need for extreme high reaction temperature which results into an ultra-fast reaction velocity; as such it is greatly useful in solid waste disposal management. In a review paper by Tang et al., [11]. The reaction temperature is required to be fast and high to enable proper thermal degradation via effective size reduction. According to Luo et al., [12], the temperature had significant influence on the pyrolysis product distribution, since the variation in the liquid yield with increasing temperature was not in a monotonic trend; it increases initially for a prevailing liquid yield; then it decreases for a prevailing thermal cracking to produce char.

This work, is aimed at catalytically converting sawdust into bio-oil in high yield via catalytic slow pyrolysis and upgrade the quality of the pyrolysis oil using locally sourced catalyst material from eggshell. To achieve this aim, we produce bio-oil from sawdust through thermal and catalytic pyrolysis processes, developed a suitable catalyst from local material (poultry eggshell) and use it to upgrade the quality of the pyrolysis oil produced for biofuel applications and finally characterize the pyrolysis oil using some techniques and compare the results with non-catalytic pyrolysis oil.

2. Materials and methods

2.1 Samples Collection and Treatment

The biomass solid (sawdust) and poultry eggshell (catalyst material) samples was obtained from Zaria-Kaduna, Nigeria. Samples were milled and oven-dried at 105-110 °C for 24 hours prior to pyrolysis. Ultimate analysis were conducted according to standard procedures. The following analyses were carried out; moisture content (wt%), volatile matter (wt%), Ash (wt%), and Fixed carbon content (wt%) in the respective samples.

2.2. Catalyst Preparation

Calcium oxide catalyst was produced from the eggshell through calcination method. Eggshell was initially washed with 1% $\text{H}_2\text{SO}_{4(\text{aq})}$ to remove dirt and stains on the shell surface. It was crushed, grounded into powder and thermally decomposed in furnace at 800 °C for 3 hours. The calcined eggshell was refluxed in distilled water at 105 °C for 6 hours. The sample was then filtered and, oven dried at 120 °C for 2 hours. The refluxed calcined eggshell was re-calcined at 800 °C for 2 hours using muffle furnace to produce fine calcium oxide (CaO) powder.

2.3. Thermogravimetric Analysis (TGA) of Sawdust and Catalyst

Thermal analysis of the biomass sample and catalyst were done by using Netch DTA/TGA instrument (with Pt and Pt-Rh Thermo couples) using calcined Al_2 as the inert standard. Initially, sample was pre-heated in a nitrogen gas flow for 15 minutes at 350 °C, then heated to 1000 °C at a 20 °C/min. The traces were recorded as weight loss versus temperature for TGA and temperature difference versus temperature for DTA.

2.4. Experimental Design

A Full Factorial Experimental Design was employed using Minitab 19 statistical software. The effect of three factors i.e., temperature (300 °C – 500 °C), a catalyst loading (10 wt% - 15 wt%) and reaction time (30 – 60 min) on the oil yield (wt%) were determined.

2.5. Sawdust Pyrolysis

Pyrolysis experiment was carried out under nitrogen atmosphere in a fixed bed tubular reactor with a length of 90 cm and an inner diameter of 8 mm, made of Stainless steel. Thirty grams (30.0g) of biomass sample (sawdust) was loaded into the reactor for 16 runs of 2 replicates temperatures either 300 °C or 500 °C. The sweep gas velocity of 100 $\text{cm}^3\text{min}^{-1}$ will be controlled and measured by a rotameter. The sample was heated at a heating rate of 10 °C/min to the final temperature of either 300 °C or 500 °C respectively and held at that temperature for 30 minutes to 1 hour or until no release of gas observed. Heating rate and pyrolysis temperature were controlled by a proportional -integral -derivative (PID) controller. This procedure was repeated with in-situ addition of CaO at 10wt% as catalyst, at the end of the experiment liquid phase was collected in a glass bottle located in a cold trap maintained at about 0°C after

pyrolysis. The biochar remained in the furnace and non-condensable gases were allowed to escape. The yield of pyrolysis liquid was calculated using the following equation (1).

$$\text{Yield (wt\%)} = \frac{\text{weight of liquid fuel (g)}}{\text{weight of total feed (g)}} \times 100 \quad \text{eqn. (1)}$$

The dense aqueous phase was characterized using FTIR spectroscopy and GCMS analysis to determine its composition.

2.6 Product Characterization

2.6.1. GCMS Analysis

GCMS analysis of the pyrolysis oil was performed (Agilent GC7890B5977MSD) at Multiuser Laboratory, Ahmadu Bello University, Zaria-Nigeria. GCMS instrument was set at 40°C min⁻¹ for 30 min. The temperature was gradually increased to 300 °C at a heating rate of 10°C min⁻¹. Elite 5 MS column was used for identifying the pyrolytic oil constituents. The pyrolysis oil was diluted with chloromethane (CHCl₃) and 1.0 uL of this diluted sample was then injected into the column. Helium was used as the carrier gas at a low rate of 0.6 mL min⁻¹. The spectra were collected at different retention times.

2.6.2 FTIR Analysis

FTIR analysis of the bio-oil sample was performed using bench top model of Agilent Cary 630 FTIR spectrometer with ATR. The liquid sample (pyrolysis oil) was analysed using the transmittance method. A small drop of pyrolysis oil was placed on the ATR crystal, and scanning was performed at a rate of 40 with a step size of 4 cm⁻¹ at the wavenumber range of 4000 – 650 cm⁻¹.

3. Materials and methods

3.1. Physicochemical properties

The results of all experiments conducted are presented and discussed. All results presented were carried out in duplicate.

3.1. Proximate Analysis of Biomass

The result of proximate analysis of the raw material is presented in table 1. The result indicated predominance of CHO (64.96 wt%), fibre (37.80 wt%), protein (8.31 wt%) and lipid (7.57 wt%) respectively. This suggested thermochemical degradation of larger molecules of lipid and protein to oil at high temperature.

Table 1. Ultimate Analysis of Sawdust

Sample ID	Moisture (wt%)	Ash content (wt%)	Lipid (wt%)	Protein (wt%)	Fibre (wt%)	CHO (wt%)
Sample A	8.35±0.40	10.2±2.01	7.31±1.01	8.75±2.11	38.2±1.33	65.39±0.53
Sample B	8.84±1.28	10.4±0.90	7.6±0.64	7.95±1.23	37.33±0.40	65.21±1.92
Sample C	8.8±1.42	10.9±1.32	7.8±1.43	8.22±0.20	37.88±2.26	64.28±0.88
Average	8.66	10.5	7.57	8.31	37.80	64.96

Ash content (10.5 wt%) and moisture (8.66 wt%) were also high. Ash and moisture are major energy reducing components of the oil, although, moisture is loss at temperature below pyrolytic condition. The presence of higher volatile matter and lower ash content indicated that the burning of fuel will be easier while presence of higher ash content act as a heat sink to absorb energy, leading to reduction in the heating value. Proximate analysis confirmed higher carbon content (2.07%-2.78%) and ultimate analysis confirmed higher carbon content (54.3%-53.5%), lower nitrogen content (2.58%-3.33%) and negligible sulfur content. The lower nitrogen and negligible sulfur content confirmed that SO_x and NO_x formation will be low during pyrolysis.

3.2. TGA and DTA Analysis of Biomass and Oil

The results TGA and DTA are presented in **Fig. 1** and **Fig. 2** indicating significant decompositions and elimination of light compounds at different stages. At the onset of the TGA, there was a slight weight loss (45.92 °C) sawdust and catalyst from a temperature of 45.92 °C to 277.78 °C and 76.01 °C to 503.98 °C respectively. The percentage weight loss recorded in this stage was 1.19% for sawdust and 5.98% for catalyst respectively. This weight loss is associated with dehydration and volatilization of low molecular weight organic substances adhered to the sawdust and CaO. The second stage shows a moderate weight loss and it commenced from a temperature of 277.78 °C to 368.87 °C for the sawdust and 503.98°C to 740.42°C for the catalyst. The corresponding percentage weight loss recorded in this stage was 20.19% and 16.29%, this is attributed to the fragmentation of higher molecular weight compounds into lower molecular weight compounds of the sawdust indicating the presence of hemicellulose and lignin [13]. The third stage of the thermal analysis of the sawdust and CaO commenced from a temperature of 368.87 °C to 500.31 °C and 740.42 °C to 859.98 °C respectively. This stage shows a severe and rapid weight loss which was recorded to be 24.18% and 34.67% for the sawdust and CaO, which could be attributed to the loss of inorganic impurities. Then the curve stabilized which indicate the end of thermal decomposition.

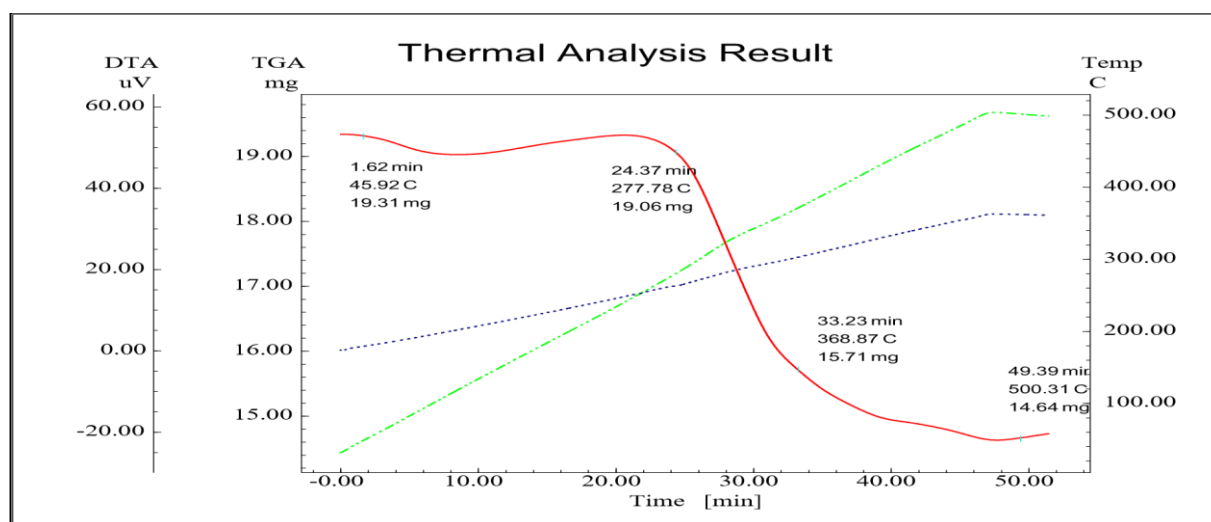


Figure 1: Thermo gravimetric Profile of Sawdust Materials

Three principle decomposition corresponding to the first exothermic peak (45.92 °C) occurs at an early stage, probably due to decomposition of bound and unbound water. The prominent decomposition peaks are proposed as second (277.78 °C) and third exothermic (368.87 °C) peaks. All these were within the ranges for lignin degradation of lignin. The first and second stages suggested exotherms resulting from chemical reactions such as oxidation, while the third stage suggested an endothermic curve resulting from a physical change. On the contrast, two stability regions are

obvious in the case of the catalyst. **Fig. 2** indicated thermal stability regions for catalyst ranges between 200 °C – 600 °C and 600 °C – 800 °C. Therefore, catalyst showed better stability than biomass, enabling complete reaction over time.

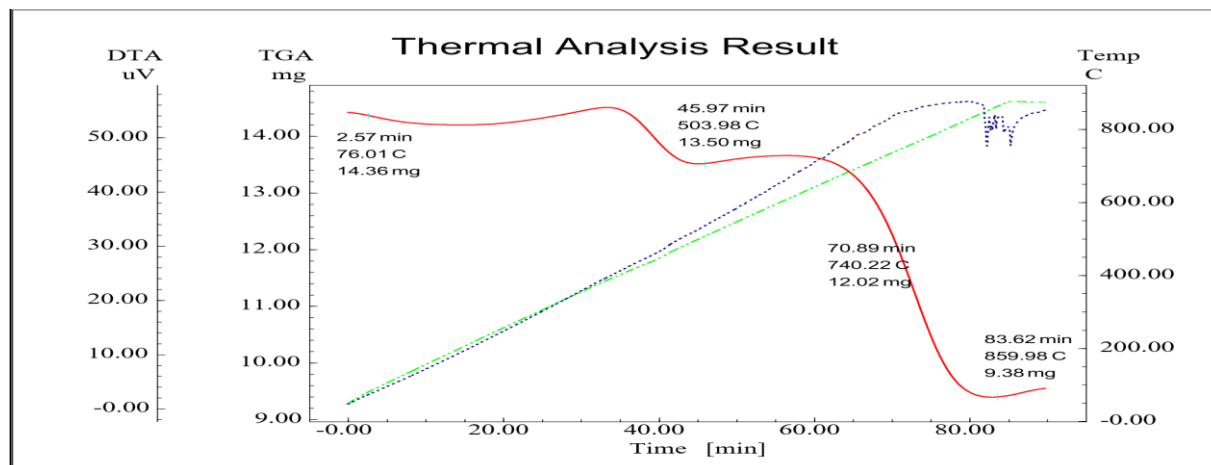


Figure 2: Thermo gravimetric Profile of Calcined Eggshell catalyst

3.3. FTIR Analysis of Oil

Results of the comparative FTIR analysis of thermal and catalytic pyrolysis oil are presented in **Fig. 3** and **Fig. 4** present the un-catalyzed and catalyzed processes respectively. The peaks at 3902.5-3831.7 cm^{-1} corresponds to the –OH group, indicating the presence of phenols, aromatics, acids, alcohols, water, and proteins impurities. The peak at 2922.2-2855.1 cm^{-1} was ascribed to the presence of C–H stretching vibration, denoting the presence of alkanes. Improved selectivity was observed for the catalysed process, especially for lower range compounds like 1° amines. Similar observations were reported by some authors.

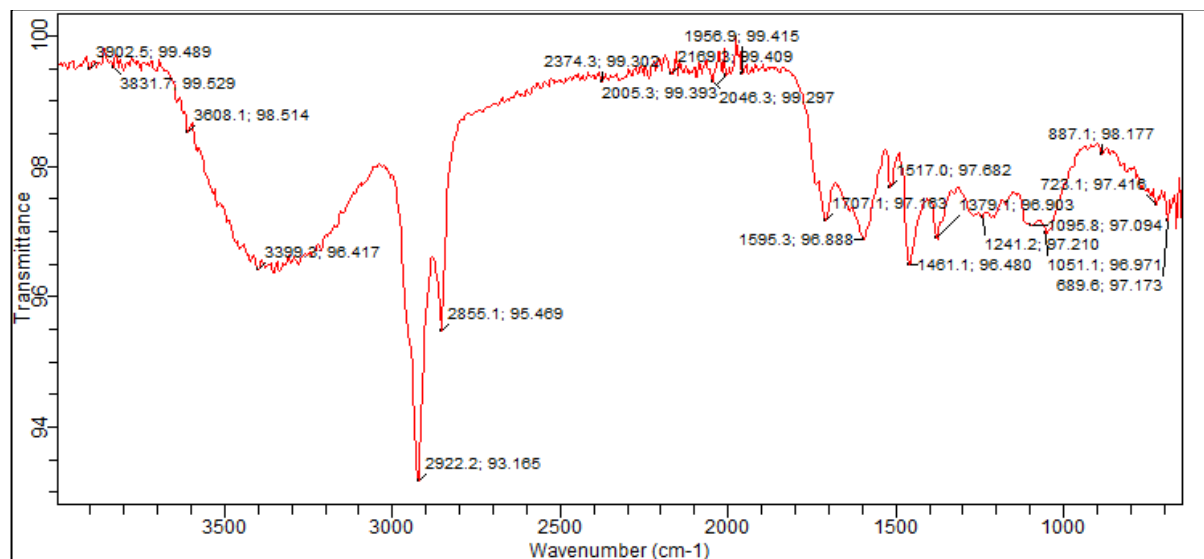


Figure 3. FTIR Analysis of Oil from Un-catalyzed Thermal degradation of Sawdust at 300 °C

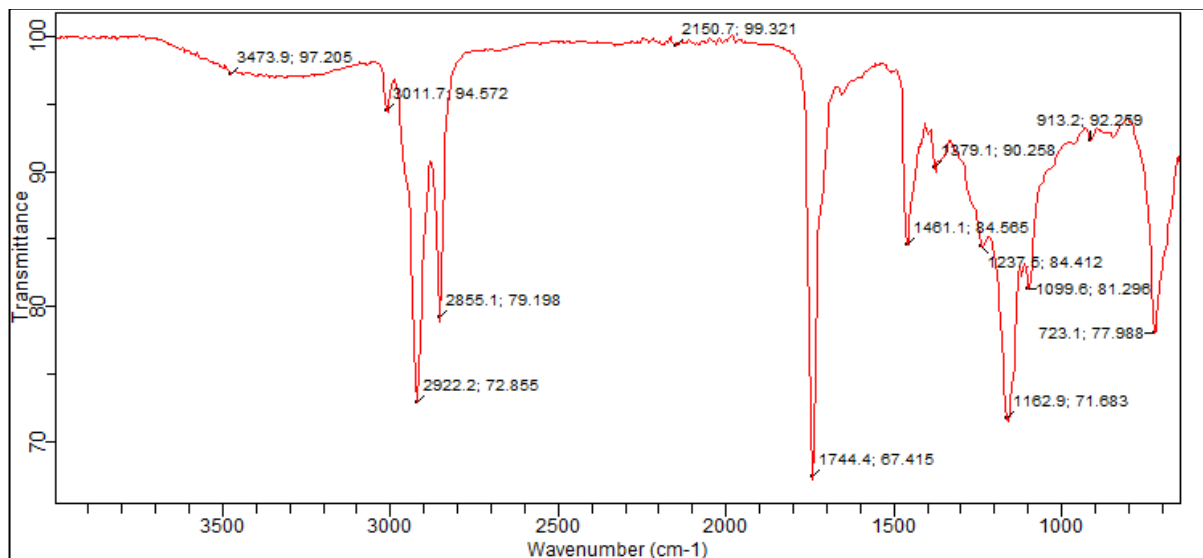


Figure 4. FTIR Analysis of Oil from catalyzed Thermal degradation of Sawdust at 300 °C

The peak at 1461-1570 cm^{-1} occurred due to the C=C bond, confirming the presence of alkynes, whereas that at 1379 cm^{-1} confirmed the presence of ester due to C-O stretching and deformation. The peak at 2169-2374 cm^{-1} was due to the presence of aliphatic cyanide/nitrile, whereas that at 1241-1379 cm^{-1} indicated the presence of alcohol. Lastly, the peak at 1744 cm^{-1} confirmed the presence of carboxylic acid, whereas that 1095-1051 cm^{-1} was ascribed to C-H plane bending, indicating the presence of aromatic compounds.

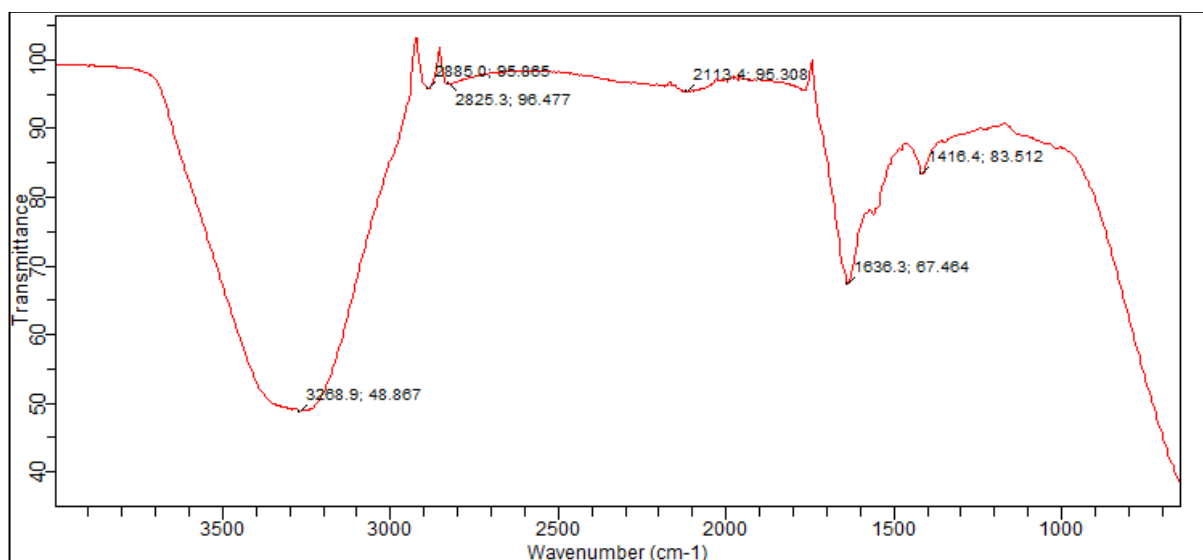


Figure 5. FTIR Analysis of Oil from Un-catalyzed Thermal degradation of Sawdust at 500 °C

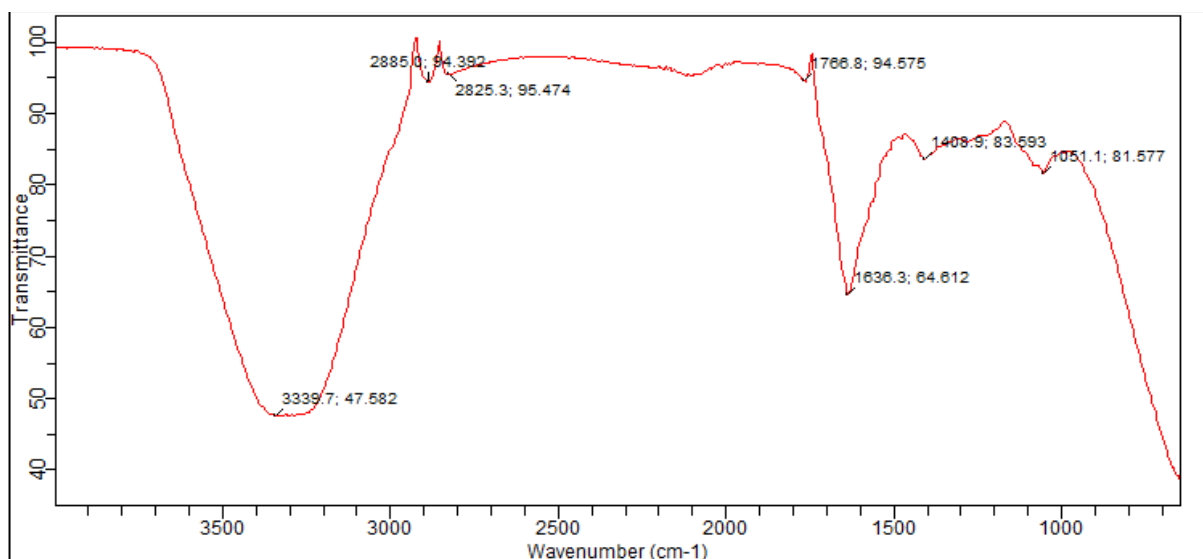


Figure 6. FTIR Analysis of Oil from catalyzed Thermal degradation of Sawdust at 500 °C

3.4. GCMS Analysis of the Pyrolysis Oil

Results of GCMS analysis was performed to identify different types of compounds present in the pyrolytic oil. Results of the comparative study of thermal and catalytic pyrolytic oils is presented in **Fig.7 – Fig. 8**. Pyrolytic oil includes almost 300 different organic compounds due to its complex nature [4]. Literature has reported among others; phenols, alkanes, alkenes, ketones, alcohols, aromatics, carboxylic acids, amides, nitriles, amines, ethers, esters, nitriles, levoglucosan, furan, and benzene are the major compounds [14] [15] [3]. From the results, **Fig. 7 and Fig. 8**, compounds are divided into six major classes: monoaromatic, polyaromatic, aliphatic, heterocyclic, oxygenated, and nitrogenated [16]. GC-MS results showed that compared with catalytic pyrolysis oil, thermal pyrolysis oil contained higher amounts of phenols, acids, esters, nitriles, alcohols, and amides and lower amounts of sulfur-containing compounds, as shown in **Fig. 8**. Thermal pyrolytic oil with high amount of phenols can be used for various chemical extraction but increased acidity due to high amount of acids decreases the heating value of the pyrolytic oil. In addition, the presence of oxygenated compounds, such as ethers, esters, and ketones may reduce the fluidity and stability of the pyrolysis oil. Although thermal pyrolysis oil with high amount of acids is useful for chemical extraction, the high acidity is a major problem for using the oil as a transportation fuel. The most important compounds present in the pyrolytic oil, such as tetra decanoic acid and octadecanoic acid, are used for making soaps and cosmetic agents and as a non-drying oil for surface coatings. N-Octadecanoic acid, known as stearic acid, is used as an emulsifying agent and solubilizing agent in aerosol products. The use of appropriate catalyst significantly increases the content of hydrocarbons, aromatics, and furfurals and reduced the content of ethers, esters, phenols, amides, nitriles, and sulfur-containing groups in catalytic pyrolytic oil. In addition, the increased amounts of alcohols and aldehydes in catalytic pyrolytic oil make it suitable to be used as transportation fuel [6]. Catalytic pyrolysis increases the acidity of pyrolytic oil, which enhances the calorific value. However, **Fig. 8** shows that the catalytic pyrolysis oil obtained in this study contained low amounts of oxygenated because during catalytic pyrolysis, oxygen reacted with hydrogen to form water, thus increasing moisture and reducing the amount of oxygenated compounds. Our result is comparable with those reported for cotton stalk, mustard stalk [17], sugarcane bagasse [18],

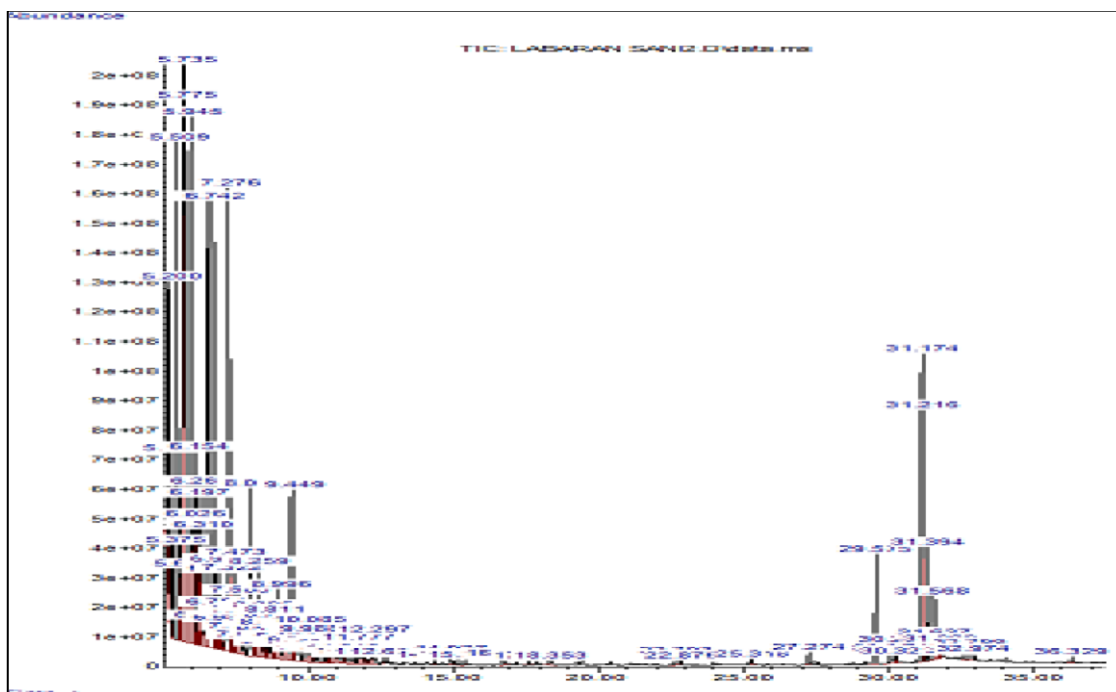


Figure 7: GCMS Profile for un-catalyzed pyrolysis at 300 °C

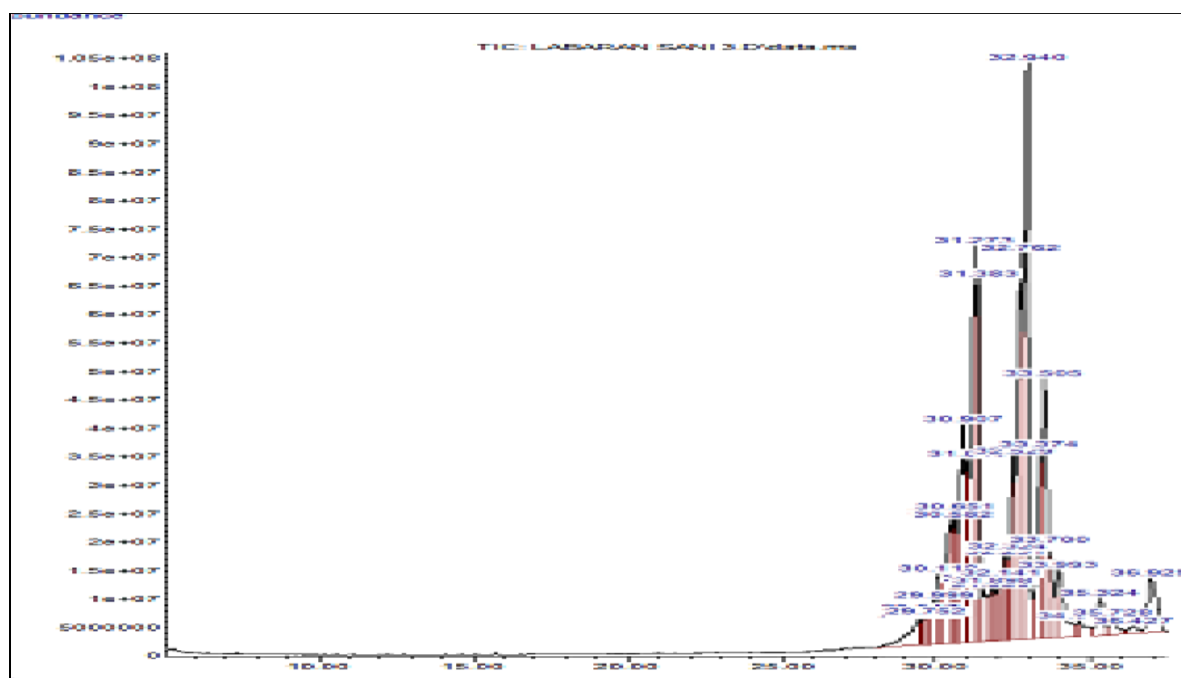


Figure 8: GCMS Profile for Catalyzed pyrolysis at 300 °C

4.4 Effect of Temperature on Bio-oil Yield from Pyrolysis

Pyrolysis is a process parameter dependant technique; therefore, process parameters optimization is essential to achieve maximum pyrolysis liquid yield. Among all the parameters, temperature, heating rate and catalyst directly affect the pyrolysis product yield. Therefore, the effects of temperature on bio-oil yield (at 10wt% catalyst loading) were investigated in this study. To optimized effect of temperature on pyrolytic end products, 300°C and 500°C were selected. **Fig. 9**, confirmed that temperature had a direct effect on the pyrolytic liquid yield. When the temperature was

increased from 300°C to 500°C, the liquid yield increased by 4.6 (wt%). At 500°C, the maximum liquid yield of 13.20 (wt%) were achieved because of complete combustion due high heat and mass transfer. Furthermore, the liquid obtained at a lower temperature (300 °C) contained the maximum percentage of acids (acetic and carboxylic acid), contributing to –OH vibration. At greater than 300 °C (e.g., 500°C), liquid and char yield decreased, whereas gas yield increased due to rapid endothermic decomposition of biomass (with a possibility of conversion of condensable gases into non-condensable gases). Various studies have reported the effect of temperature on pyrolysis yield. For example, pyrolysis yield of soybean cake, achieved only 11.82 (wt%) extra biomass conversion by increasing the temperature from 400 °C to 700 °C [19]. Consistent with the results of these studies, our results indicated that biomass conversion increases with the increase in pyrolysis temperature.

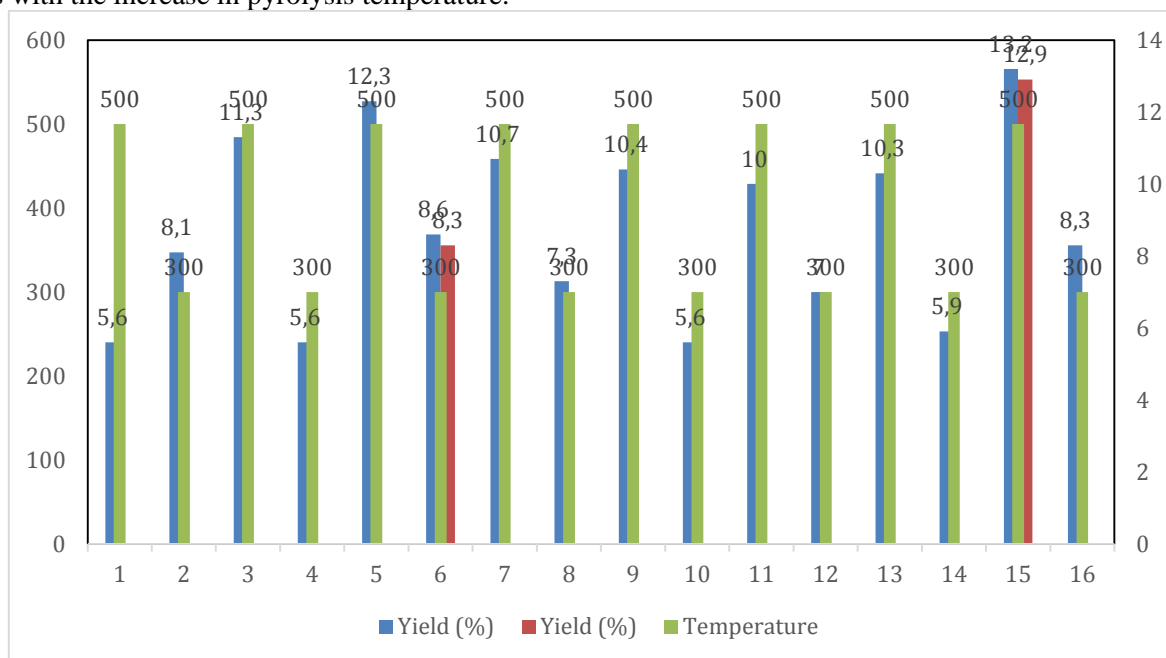


Figure 9: Effect of Temperature on the Bio-Oil Yield from Pyrolysis

Conclusion

In this study, thermal and catalytic pyrolysis of sawdust and physicochemical characterization and preparation of suitable catalyst from local material (eggshell) was carried out. The catalytic pyrolysis results confirmed decreased in pyrolytic liquid yield at 10 wt% catalyst loading over noncatalytic pyrolytic liquid yield. FTIR analysis revealed the presence of various useful functions groups which confirmed the existence of aromatics, phenols, alcohols, ethers, esters and aldehyde. GCMS results confirmed that the use of catalyst enhances the properties of pyrolytic oil. Also, it was noticed that produced acid during non-catalytic pyrolysis got converted into ester during catalytic pyrolysis. Further, catalytic pyrolysis oil showed superior fuel properties over non-catalytic pyrolytic oil by means of reduction in the oxygen content, hydrocarbon distribution and acidity. Based on the above results, it can be concluded that eggshell can be used to develop a suitable catalyst from local material to improve the quality of pyrolysis oil. The optimum temperature to produce pyrolysis oil using the formulated catalyst at 10 (wt%) was 500 °C.

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