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Bio oil production from Agro waste residue: Thermochemical conversion to improve oil quality

K Midhun Prasad[1] and S Murugavelh[2*]

[1]School of Mechanical Engineering
[2]CO_2 Research and Green Technology Centre
Vellore Institute of Technology, Vellore – 632014

E-mail: midhunprasad.k@vit.ac.in, Murugavelh.s@vit.ac.in

Abstract. Energy is the symbol of economical developments and human settlements. This study is carried out to find the effect of oil yield by optimization of temperature and residence time for the thermochemical conversion of solid waste into the liquid fuel by pyrolysis reaction in an auger reactor made of stainless steel with the heating rate of 10 ˚C/min with the maximum temperature range of 1000 ˚C. The agro waste of Tomato plant are left in land after harvesting which can be converted into usable carbon neutral liquid fuel by further processing. The experiment is carried in a different temperature ranges from 450, 500, 550, 600, 650 ˚C. Tomato plant is collected, dried in open solar drying until the sample weight remains constant to remove the bound moisture content. Then crushed into small pieces, and subjected to thermogravimetric analysis, proximate and ultimate analysis. Further the bio oil is characterised with GC-MS and FTIR to find the compounds present. The moto of this study is to find the convert the waste into high energy content liquid fuel.

1. Introduction
World today focused in the search of alternative fuel to overcome the usage of fossil fuels. The culture nowadays is infrastructure with using of huge amount of fossil fuels without knowing the drawbacks [1]. Increase in the threat on environmental pollution and other issues becomes the serious effects nowadays. The major cause of environmental pollution results in the exhaust from automobiles because of using of fossil fuels which associates with CO_2, NO_x and SO_x. Future is dependent on alternative fuel which can helps in production of clean energy. One of the solutions for the production of alternative fuel is based on the biomass and agricultural waste residue [2]. Biomass can be used as an alternative source for the energy fuel generation in the present scenario. Pyrolytic conversion of waste left out after crop harvesting can be utilised. Tomato is harvested in other regions all around the world, the plant was then left of the land for the natural decomposition or burned in the land. Burning also create the problem with environmental issues, so collecting those and using is user friendly way can be approached [3]. Pyrolytic conversion of waste biomass to liquid fuels has a significant in the climate change problems which associated with reducing the CO_2 emission also consider as a better replacement for fossil fuels.

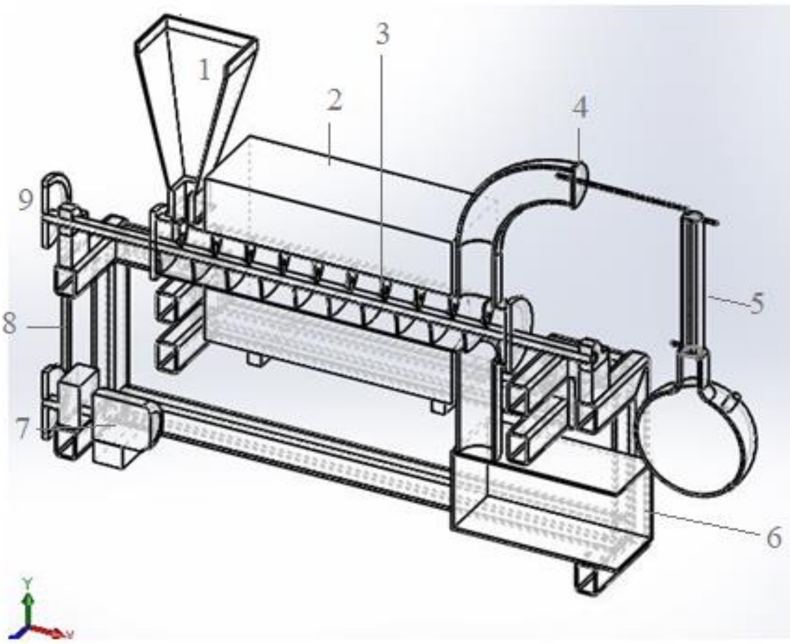
India is a country which major population depend on agricultural activities focusing on the waste generated can help in the larger quantity production of valuable by products, which can be of solid, liquid and gases [4]. The obtained liquid is pyrolytic oil which can directly use in boilers and turbines on upgradation this can be use as a high-quality hydrocarbon fuel [5]. Whereas biomass also emits little amount of sulphur and nitrogen, which is less when compared to the fossil fuel emissions.

Among the other thermochemical conversion process pyrolysis is one of the better energy production process. Thermal degradation of waste solids and biomass in the absence of oxygen in a closed reactor is called pyrolysis. In olden days pyrolysis is used for the charcoal production [6]. More attention has been gained to the pyrolysis process due to it efficiency in converting solid to liquid fuels, also this technology helps in generation of high fuel to feed ratio. There are basically three types of energy extraction process combustion, gasification and pyrolysis [7]. In pyrolysis the effect of temperature starts around 350 ˚C to 550 ˚C and keep on increasing to the maximum temperature of 900 ˚C in an absence of oxygen [8]. During the high temperature the biomass starts cracking long molecular chain of carbon, hydrogen and oxygen breakdown into short chain compounds in gaseous and char form [9].

In this study optimization of temperature for the efficient liquid yield was carried out using tomato plant waste in a auger reactor at the retention time of 2 min with varying temperature ranges from 450 ˚C, 500 ˚C, 550 ˚C, 600 ˚C and 650 ˚C, the experiment was carried out at the heating rate of 20 ˚C min^{-1}. The obtained liquid is collected and analysed with GCMS and FTIR.

2. Experimental Setup

Pyrolysis process is carried out using a closed auger reactor made of stainless steel with the maximum feedstock holding capacity of 5 kg specifically designed for batch process, with a variable heating rate



1.	Feed hopper	4.	Pyro gas exit	7.	Step down motor
2.	Furnace	5.	Condensing column	8.	Transmission chain
3.	Screw feeder	6.	Char collection chamber	9.	Shaft

Figure 1. Experimental Setup

and temperature range up to 1000 ˚C. The entire setup is compactly packed the feed is feeded at the hopper and char is collected the chamber below shown in figure 1. The shaft speed is adjusted by step down gear box. At the end of the reactor the char is collected down and the gas produced at the top. The gas obtained is then flow through a water-cooled condenser column where the temperature of the water is maintained at 8 ˚C for the proper condensation.

3. Materials and method

The experiment is carried out using tomato plant waste, the biomass is collected from local farmers from Vellore. The sample is then washed to remove sand and dirt present and dried in open solar drying until the weight drop occurs. Then the sample is milled to the size less than 2 mm for the analysis.
The elemental analysis of tomato plant (leaf, steam and root) was carried out using PerkinElmer 2400 model asper ASTM standards. Proximate analysis was equipped to find the moisture content, ash content, fixed carbon and volatile matter by ASTM norms using hot air oven, muffle furnace and weighing balance. Cellulose, hemicellulose and lignin content present in the sample was analysed by Van Soest method. Thermogravimetric analysis of feedstock is analysed using Mettler Toledo in a nitrogen atmosphere at the flow rate of 20 ml min^{-1}. The TGA experiment was carried out from the range of atmospheric temperature to 800 ˚C with a constant heating rate of 20 ˚C min^{-1}. The oil obtained is then analysed with GCMS and FTIR to find the functional group and compounds present in the sample, calorific value of the sample is found by bomb calorimeter.

The operation parameter of the experiment was optimized the temperature range from 450 ˚C to 650 ˚C and fixed other parameters for the other set of experiments, retention time of 2 min with the fine particle size (2 mm) and constant heating rate of 10 ˚C min^{-1}.

4. Results and Discussion

Table 1. Biomass characterisation

Proximate Analysis		**Ultimate Analysis**		**Composition analysis**	
Moisture (wt%)	10.2	C (wt%)	38	Hemicellulose (wt%)	28.8
Ash (wt%)	8.08	H (wt%)	5.2	Cellulose (wt%)	39.1
Fixed Carbon (wt%)	51.06	N (wt%)	2.7	Lignin (wt%)	12.1
Volatile Content (wt%)	30.12	S (wt%)	1.1	-	-
Calorific Value	21 MJ/kg	O (wt%)	41.1	-	-

Pyrolysis of tomato plant waste is carried out at the different temperature range trials from 450 ˚C, 500 ˚C, 550 ˚C, 600 ˚C and 650 ˚C to find the better liquid yield, at the initial stage the reactor is set to the temperature and the sample is feeded into the reactor in an inert atmosphere absence of oxygen, the retention time of the reaction was optimized to 2 min. The gas produced was condensed and the liquid and char obtained was collected then measured, uncondensable gas calculated by difference Table1 describes the proximate which shows the presence of moisture content, ash content, fixed carbon, volatile matter and ultimate analysis of the sample shows the presence of carbon, hydrogen, nitrogen, sulphur, oxygen presence in the feedstock sample. The biomass is also analysed with hemicellulose, cellulose and lignin content present shown in table 1.

4.1 TGA

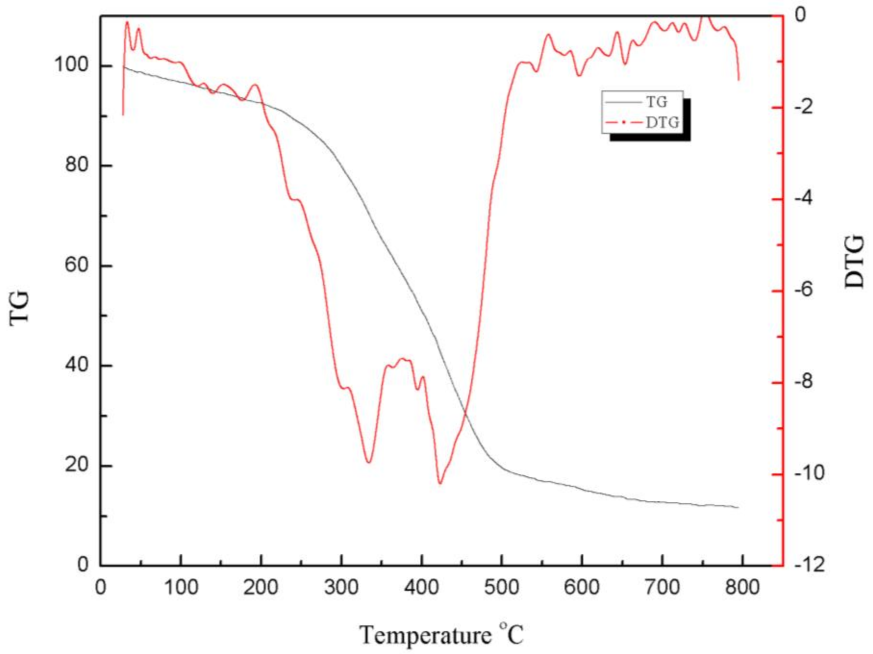


Figure 2. TGA

Thermogravimetric analysis of tomato plant waste was carried out to find the behaviour of thermal decomposition. Figure 1 shows the degradation curve of the feedstock at 20 ˚C min^{-1}, at the initial stage 10 mg of sample is taken in a crucible and the weight loss at the varying temperature is noted. A slight drop around 100 ˚C denotes the presence of bound moisture. Thermal degradation at the second zone starts at 200 ˚C to 500 ˚C. And the final stage in the degradation occurred at the temperature range of 500 ˚C to 650 ˚C. After reaching at the high temperature the curve become constant. The three zones in degradation denotes the decomposition of cellulose, hemicellulose and lignin.

4.2 Influence of temperature

Change in temperature has a direct impact on the by products yield form the tomato plant pyrolysis. From the analysis it is noted that increase in the temperature leads to the decrease in the liquid and char yield this impact in the increase in the gases yield. The decrease in liquid yield leads to the thermal cracking of biomass at the higher temperature, also increase in this temperature results in higher gas production. Table 1 and figure 3 shows the yield percent of liquid, solid and char. It is observed that pyrolysis at 600 ˚C is the efficient range to obtain higher liquid yield and for better gases yield 650 ˚C is the optimum range where it produces up to 45.4 wt% of gases compounds.

Table 2. Effect of Temperature

Yield	450 ˚C	500 ˚C	550 ˚C	600 ˚C	650 ˚C
Solid	56.5	54.1	39.8	30.0	29.8
Liquid	26.44	24.0	21.5	33.6	24.8
Gases	17.06	21.9	38.7	36.4	45.4

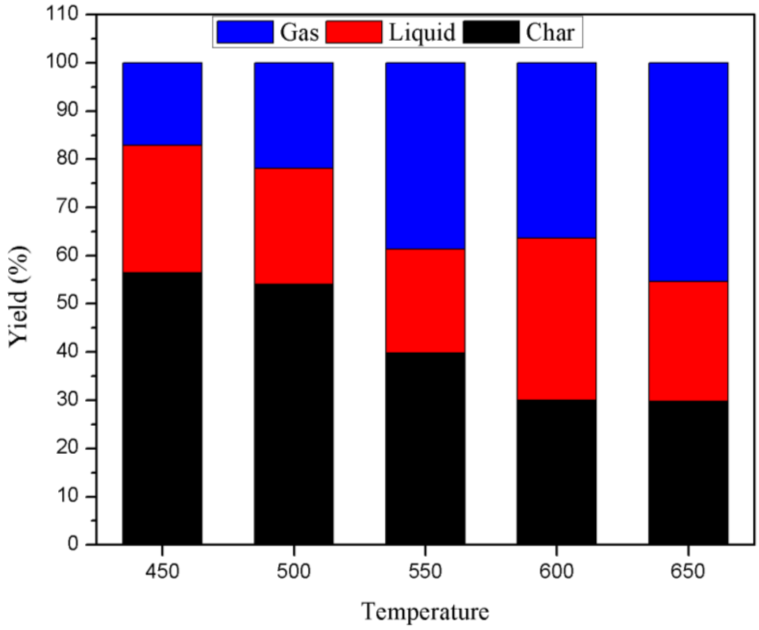


Figure 3. Yield Percentage

4.3 GCMS analysis of bio oil

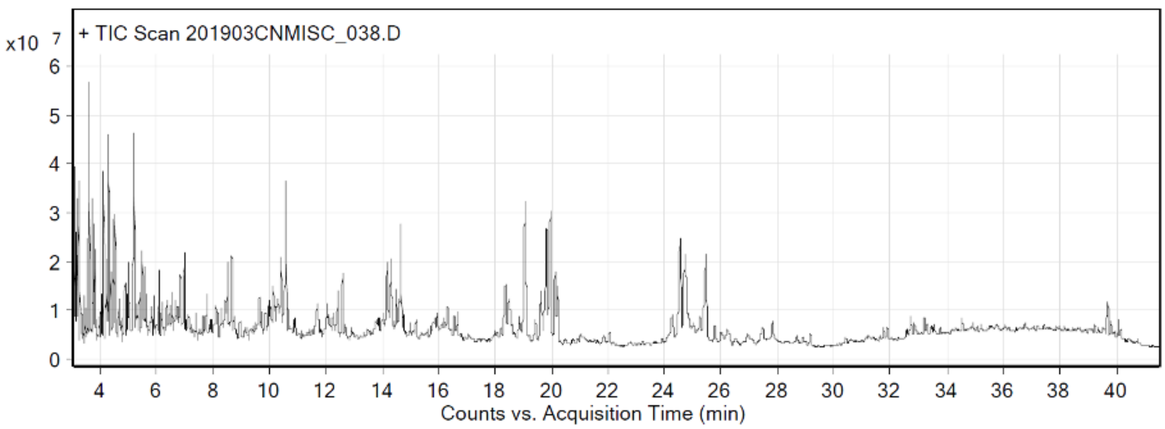


Figure 4. GCMS of bio oil

GCMS of the oil sample was analysed to find the compound group present in the sample, this helps in analysing the compound group present in the sample. It is equiped with GCMS- QP 2010 SHIMADZU analyser, operates at the temperature range from 70 ˚C to 300 ˚C in an helium atmosphere. From the figure 4 it is observed that most of the peak found at the range of 1 to 6 and minor peak found at the entire range, the compounds present in the sample was given in table 2 below. The compound present in the oil sample contains mostly flamable compounds like indane, indene, benzene, p – xylene, Silane etc, most of the compounds found are highly flammable in nature.

Table 3. GCMS compound table

S.no	RT	Compound Name
1	3.124	Benzene
2	3.238	p-Xylene
3	3.432	Cyclopentene
4	3.703	Octane
5	3.927	Indene
6	4.023	Indane
7	4.128	Phenol
8	4.735	Cyclopentasiloxane
9	5.233	Naphthalene
10	5.489	Cyclododecane
11	6.617	1H-Indene
12	6.923	Silane
13	7.396	Naphthalene
14	8.663	Tetradecane
15	9.482	Bicyclo
16	10.41	n-Pentadecanol
17	12.393	Fluorene
18	12.934	Hexadecane
19	14.65	Heptadecane
20	16.679	Hexadecane
21	19.837	Oleanitrile
22	21.849	Cyclohexadecane
23	24.548	Eicosane
24	25.454	Octadecanenitrile
25	26.213	Methyl stearate
26	28.667	Behenic alcohol
27	28.892	Docosane
28	31.756	Tricosane
29	33.554	Tetracosane
30	35.784	Pyrrolidine

4.4 FTIR

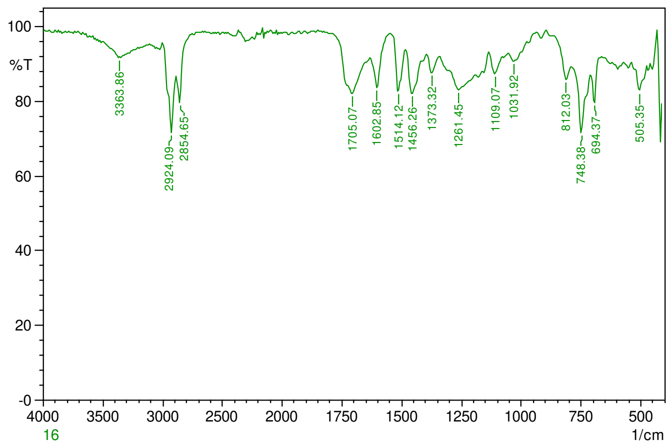


Figure 5. FTIR of bio oil

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FTIR of the bio oil sample is analysed to found the organic, inorganic and polymers present in the sample. FTIR spectra was carried out from 500 – 4000 cm^{-1} equiped with Perkin Elmer analyser. From the table it is observed that peak corresponds to the vibrations. The peak at 505 denotes the presence of aromatic compounds, peak at 1031 denotes the presence of epoxi group, peak at 1373 coresponds to the presence of alkenes group and the peak at the range 1700 represents the presence of carboxylic acids, finally the peak at 3363 denotes the presence of N-H bending denotes the presence of amines and amides.

Table 4. Functional group using FTIR

Wave number (cm^{-1})	Vibration	Functional group
400 - 600	C-H Bending	Aromatic
980 -1200	C-O Stretching	Epoxide
1250 - 1300	C-O Stretching	Carboxylic Acid
1350 - 1500	C=C Bonding	Aromatic ring
1500 - 1550	C=C Bending	Alkenes
1600 – 1620	C=O Bonding	Aldehydes, Ketones, Carboxylic acids
1700 - 1725	C-OH Stretching	Carboxylic Acid
2854	C-H Bending	Alkanes
2924	C-H Stretching	Alkanes
3363	N-H Bending	Amines, amides

5. Conclusion

This study was carriedout to find the optimization of temperture for the better oil yield using tomato plant waste left after harvesting. The experiment was conducted with different temperature ranging from 450 ˚C to 650 ˚C, it is noted that 600 ˚C is the maximum optimum temperature for better oil yield. The calorific value of the oil was found to high compared to the biomass. GCMS and FTIR reported that the oil has more number of flamable compounds like benzene, p-xylene, cyclopentene, octane, indene, indane and Naphthalene. Presence of this compounds helps in increasing the calorific value of the oil sample

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