

# Recycling of Plastic Wastes in Tiruvannamalai City: Thermal Cracking of Waste Plastic into Gasoline Products under Various Operating Conditions

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**Abstract** Due to the environmental threats of municipal plastic waste generation, plastic waste is obvious to recycle for a satisfying plastic-free environment. Lots of techniques are available for plastic waste recycling; however, the thermal cracking was found as a powerful technology to decrease plastic waste pollution simultaneously, producing petroleum-derived products. The objective of this investigation is to convert high-quality gasoline fuel from the plastic-based glucose bottles (GB) by the thermal cracking process at moderate reaction conditions. In this investigation, the waste plastic was thermally cracked in a batch reactor at a temperature range between 350-500°C, and the reaction time varied from 60-120 min, respectively. As a result, the most extreme yield percentage of liquid fuel 72.80% was obtained at an optimum temperature of 450°C and 90 min of reaction time. The derived liquid fuel contains mainly of aromatic functional groups (C=C stretch), and that is made out of gasoline-range hydrocarbons with a carbon number of C<sub>4</sub>-C<sub>28</sub>. Henceforth, the produced liquid fuel was termed as aromatic liquid hydrocarbon fuel (ALHF), and that would be recommended for use as commercial gasoline fuel.

**Keywords:** *glucose bottle, thermal cracking, GCMS, FTIR, ALHF, gasoline-range*

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## 1. Introduction

Plastic is an essential item in our regular day-to-day existence for over the last three decades and is ubiquitous around us. Due to their scope of applications in various sectors, the plastic waste generation has continuously expanded to suit modern lifestyles [1]. Aside from the food and paper waste generation in municipal solid wastes (MSW), plastics have a significant part in MSW representing, 8-12% by weight [2]. The global generation of plastics during 2018-19 reached 150 million Tonnes/Annum (TPA), of which India generated 9.4 million TPA [3]. Around 50-70% of plastic wastes in the MSW are in the form of packaging items and it is composed of 7% of Polyethylene terephthalate, 35% of Polyethylene, 13% of Polyvinylchloride, 23% of Polypropylene, 10% of Polystyrene, and 12% of other plastics. In Tamilnadu, the plastic waste generation was approximately 431472 TPA, out of 94% could be segregated by local bodies, and only 6% (268.575 TPA) were recycled [4].

Plastic waste disposal has become a major concern of developing cities such as Tiruvannamalai city, in the Tamilnadu state of India. In the earlier years, the

Tiruvannamalai city faces a challenge on plastic waste disposal. Several disposal solutions exist to deal with the growing plastic wastes, mainly landfilling, Incineration, mechanical and chemical recycling. Be that as its way, some of these disposal modes pose a severe threat to the environment [5]. Plastic wastes are widely being landfilled, which cannot keep up with the waste generation rate. Incineration leads to poisonous emissions such as Polychlorinated Biphenyls (PCBs). Mechanical recycling is only applicable to certain plastics and a limited number of times, where eventually, these recycled plastics end up being non-recyclable [6]. These techniques are economically high costs, energy-intensive, and produce low-grade products excluding chemical recycling [7]. Chemical recycling is one of the most efficient methods for converting waste plastic into value-added fuels such as Liquid and gaseous fuels [8]. Chemical recycling is also termed as thermal cracking or pyrolysis. Pyrolysis is an endothermic process, which involves the thermal degradation of plastics by heating them to a higher temperature range between 350-900°C in an oxygen-devoid atmosphere. The product formed at the end of pyrolysis depends on set-up process parameters such as the type of feedstock, reaction temperature, reaction time, operating pressure, heating rate and so forth [9,10,11].

Numerous researches have been researched with respect to the potential of plastic pyrolysis processes for value-added fuel production. It must be noticed that the pyrolysis product yield quantity and quality mainly depend on feedstock composition, operating conditions, and reactor configuration. Therefore, this research work deals with plastic pyrolysis process in a batch pyrolytic reactor and exploring their process optimum conditions to maximize fuel quantity and improve fuel quality. The liquid fuel quality was accessed through Fourier transform infrared spectroscopy and Gas Chromatography with Mass spectrometry analyses.

## 2. Material and Methods

### 2.1. Pre-processing and Identification Test of Feedstock Material

In this investigation, the plastic-based glucose bottle (GB) was selected as a feedstock material, and it was primarily collected from Tiruvannamalai Municipality. The collected waste plastic was then washed successively with alkaline detergent followed by shredding into a small size of 2cm<sup>2</sup>. The shredded plastic was then dried under the sun drying, and it allows identification tests for affirming the plastic groups. Identification tests for the plastic materials are outlined in Table 1.

Table 1. An identification tests of various plastic materials

Test	PE	PP	PS
<b>Water</b>	Floats	Floats	Sinks
<b>Burning</b>	Blue flame with yellow tip, melts and drips.	Yellow flame with blue base.	Yellow, sooty Flame and drips.
<b>Smell after Burning</b>	Like candle wax	Like candle wax less strong than PE	Sweet
<b>Scratch</b>	Yes	No	No

The elemental compositions in the feedstock material were analyzed by using Elementar Vario-III (CHNS Mode) analyzer. The thermal behavior and degradation mechanism of feedstock material was carried out by a simultaneous thermo-gravimetric analysis and different thermogravimetric analysis using TA Instruments Trios V5.0.0.44616 under controlled conditions. The following formulae can calculate the higher heating value (HHV) and the lower heating value (LHV) of feedstock;

$$\text{HHV} = (0.3491 * C) + (1.1783 * H) + (0.1005 * S) - (0.1034 * O) - (0.015 * N) - (0.0211 * A) \quad (1)$$

$$\text{LHV} = \frac{\text{HHV} - 2.442 * (8.936 * H)}{100} \quad (2)$$

The H/C ratio can determine the existence of hydrocarbon compound in feedstock material. The following formulae can calculate the H/C ratio,

$$\text{H/C Ratio} = \frac{\% \text{ of C in Feedstock}}{\% \text{ of H in feedstock}} \quad (3)$$



Figure 1. MSW dumping site in Tiruvannamalai Municipality



Figure 2. Glucose bottle wastes after shredding

### 2.2. Experimental Setup and Procedure

The process involved thermal cracking of plastic waste has been carried out in a batch pyrolytic reactor and its experimental set-up as shown in Figure 4. A batch reactor has a 2kg capacity, which permits a temperature level up to 1000°C using the band heater and that was controlled and sensed by a PID controller and temperature sensor respectively. A purging of nitrogen gas in the reactor is even preventing the harmful contaminants or gases. A shell and tube condenser made by stainless steel with the copper tube was fixed at the reactors out. Before experimentation, precisely measured 250gms of feedstock material (GB) was loaded to the reactor and the reactor was heated in the temperature between 350-500°C with a 10°C/ min increment. After preceded the experimentation, the vapour produced from the reacting chamber was then condensed into pyrolysis liquid oil using shell and tube condenser with re-circulated water provisions. The operating time of every trial was monitored from the primary drop of the liquid-vapour produced. A bottom product such as char-residue was taken out from the reacting chamber after completion of the experiment.

After completing the experiment, a mass balance of pyrolysis products was estimated by the following empirical equations.

$$\text{Liquid yield (wt.\%)} = \frac{\text{liquid yield produced (Wl)}}{\text{Mass of GB fed (Wf)}} \quad (4)$$

$$\text{Pyro gas Yield (wt.\%)} = \frac{\text{Gaseous Yield produced (Wg)}}{\text{Mass of GB fed (Wf)}} \quad (5)$$

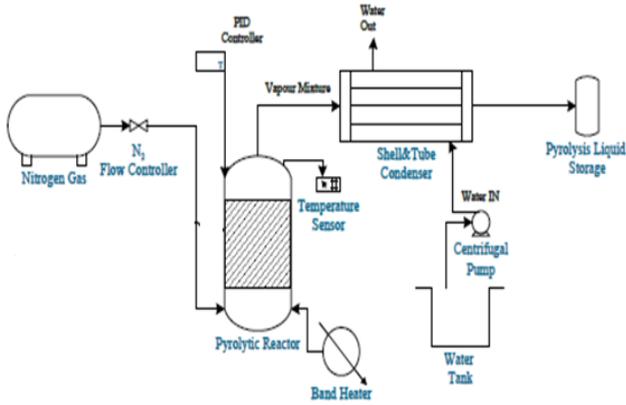


Figure 3. Flow sheet representation of Plastic Pyrolysis process



[a-Batch reactor; b-Heater; c-Sensor; d-Condenser; e-Water In; f-Water Out; g-Nitrogen (Purging Gas); h-Control Valve; i-PID controller; j-Water Tank; k-Liquid Collection Point].

Figure 4. Experimental setup of Pyrolysis process

### 2.3. Characterization of Liquid Fuel Oil

The liquid product yield was characterized by using FT-IR spectra and GC/MS analyses to observing the functional group and the hydrocarbon compound presence in the obtained liquid product. In order to obtain the functional group and its typical molecular structure, the liquid fuel was analyzed within the wavenumber between 500-3500  $\text{cm}^{-1}$  and resolution number 5  $\text{cm}^{-1}$ . The GC/MS analysis was used to found the hydrocarbon compound present in the obtained liquid product.

## 3. Results and Discussion

### 3.1. Grouping Tests and Characterization of Feedstock Material

The following identification tests of raw feedstocks were conducted on before the pyrolysis experiment for affirming the plastic groups and obtained results were discussed below;

- Initially, a few pieces of raw feedstock (GB) were floating on the **water** surface; it would be demonstrative that the raw material may contain either polyethylene or polypropylene.
- After that, about 2gms of raw feedstock (GB) were **ignited** quite readily and showed blue edges around the yellow flame.
- A distinct **smell** of candles was observed burning. Hence, these tests confirmed that Glucose bottle waste belongs to polypropylene plastic.

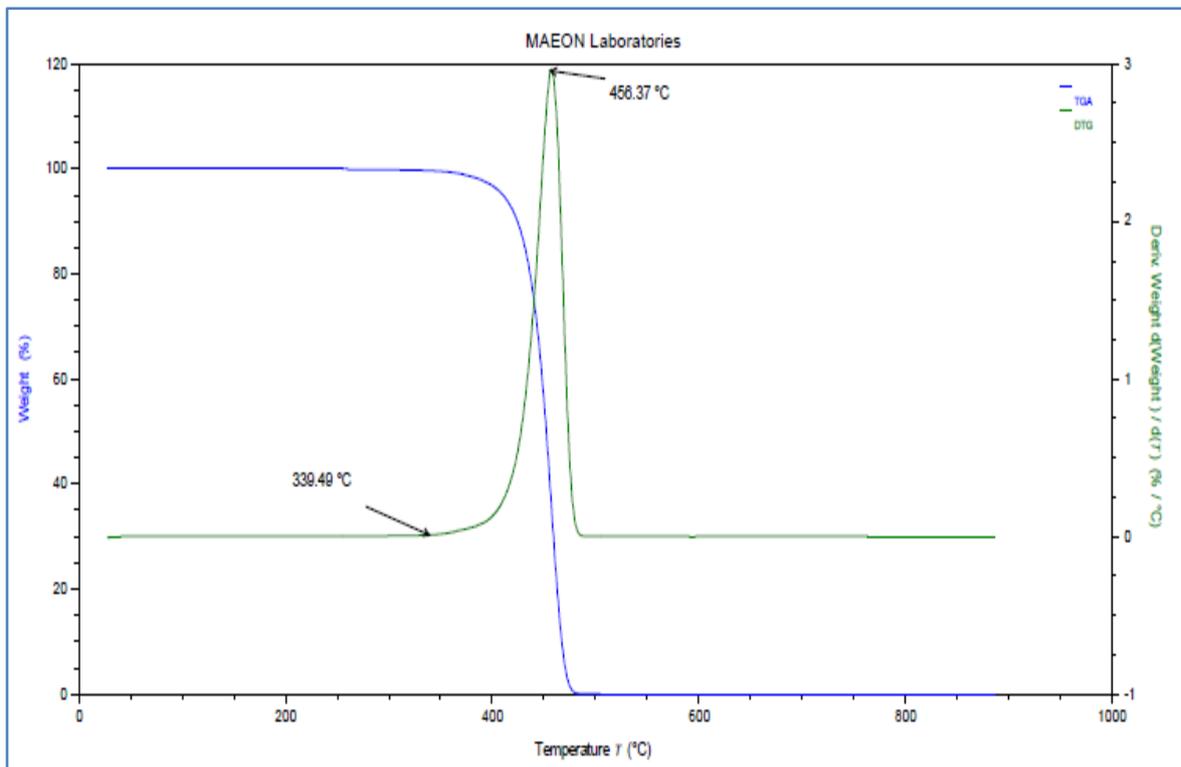


Figure 5. TGA-DTG curves of waste GB at 10°C/ min

The percentage of elemental compositions in waste plastic material (GB) such as carbon, hydrogen, nitrogen, sulphur, and other contents were characterized **Elementar Vario-III analyzer**. The carbon and hydrogen contents are imperative parts of producing the maximum quantity of hydrocarbon products. As expected, elemental composition has a major part of carbon and hydrogen percentage up to the value of 80.82 and 14.05 respectively. The Higher heating value (HHV) and Lower heating value (LHV) of waste glucose bottles were determined by Eqns. (1) and (2), which values are indicated that 44.82 MJ/Kg and 53.21 MJ/kg respectively. The evidence of existence hydrocarbon range in the waste glucose bottle can be assessed by an Eqn. (3). The hydrocarbon ratio of waste glucose bottle was found to be 5.752 and also saturation level was indicated that the C-C bonds are strong. Moreover, it was interesting to notice that the ash content of raw feedstock was 0.00, which is most favourable for producing the maximum quantity of liquid yield [12]. The thermal degradation of waste feedstock material (GB) was analyzed using a simultaneous thermo-gravimetric analysis with different thermo-gravimetric analysis (TGA-DTG).

Figure 5 shows the normalized weight loss of the feedstock as a function of degradation temperature. The degradation of feedstock material was showed single-stage thermal degradation mechanisms, which occurred in the temperature range between 339.49°C to 456.37°C. The complete conversion (T-100%) of feedstock material was achieved until 456.37°C. J. Nisar *et al.* 2019 studied thermal analysis of polystyrene at different heating rates and reported that the temperature increases from 387°C to 428°C [13].

### 3.2. Factor Affecting Thermal Cracking Process

In order to optimize the reaction temperature and time for the thermal cracking of waste plastics in a batch reactor at a temperature range between 350-500°C and reaction time was varying from 60-120 min respectively. The factors influencing the thermal cracking process for liquid product yields were discussed in the subsections.

#### 3.2.1. Reaction Temperature

In the thermal cracking of the waste plastic (GB), the operating temperature significantly impacts on the pyrolysis liquid product yield. In order to know the optimum temperature, the waste plastic (GB) was thermally cracked at the temperature range between 350-500°C, for producing maximum liquid products under controlled conditions. The effect of reaction temperature on GB degradation demonstrated that, the maximum quantity of liquid yield was observed at 450°C and their yield percentages were found to be 72.80 % of liquid yield, 15.51 % of pyro gas and 11.69 % of char residue respectively. At the temperature ranges between the 450°C-500°C, was most favourable for gaseous or char products. The obtained results are in reasonable agreement with previous researcher's report [4,13,14].

#### 3.2.2. Reaction time

The reaction time is also shown as a key factor that impacts the pyrolysis product distributions. The effect of reaction time on thermal cracking of the waste plastic (GB) was investigated by varying operating time from 60-120 min at an optimum temperature of 450°C. The results showed that, the reaction time of 90 min is an optimum reaction time for producing a maximum amount of liquid yield of 72.80 %. Further increase in the reaction time from 90-120 min, which is most suitable for pyro gas production and the pyrolysis product yields at a reaction time of 120 min, was found to be 70.14 % of the liquid yield, 19.80 % of pyro gas and 10.06 % of char residue respectively. The observed results are in good association with reported literature [13,14,15].

### 3.3. Characterization of Liquid Fuel

#### 3.3.1. FTIR Analyses of Liquid Fuel

FTIR analysis of liquid fuel obtained from the waste GB thermal cracking as shown in Figure 6. The following types of functional groups are appeared in the Perkin Elmer spectrum, such as wavenumber 3648.79  $\text{cm}^{-1}$  shows that the presence of alcohols functional group in medium sharp appearance with respective to O-H stretch, wavenumber 3311.88  $\text{cm}^{-1}$  shows that the presence of alkynes functional group in strong sharp appearance with respective to  $\equiv\text{C-H}$  bend, wavenumber 2923.77  $\text{cm}^{-1}$  shows that the presence of alkanes functional group in strong appearance with respective to C-H stretch, wavenumber 2855.88  $\text{cm}^{-1}$  shows that the presence of alkanes functional group in strong appearance with respective to C-H stretch, wavenumber 1702.82  $\text{cm}^{-1}$  shows that the presence of aromatic compound functional group in weak appearance with respective to C-H bend, wavenumber 1460.31  $\text{cm}^{-1}$  shows that the presence of alkanes functional group in strong appearance with respective to C-H bend, wavenumber 980.32  $\text{cm}^{-1}$  shows that the presence of alkenes functional group in strong appearance with respective to  $\text{C}=\text{C}$  bend, and wavenumber 489.95  $\text{cm}^{-1}$  shows that the presence of alkyl halides functional group in strong appearance with respective to C-I stretch. Also, it was observed that appearing groups in the FTIR spectrum are mostly contained aromatic functional groups in the range  $-\text{C}=\text{C}$  stretch.

#### 3.3.2. GC/MS Analyses of Liquid Fuel

GC/MS analyses of liquid fuel obtained from the waste GB thermal cracking process as shown in Figure 7. The following hydrocarbon compounds were showing in the liquid fuel obtained from waste GB thermal cracking. According to the retention time 5.121 compound is Cyclohexene, 4-methyl ( $\text{C}_4\text{H}_{10}$ ), retention time 5.335 compound is 1-Pentanol, 2-methyl-acetate ( $\text{C}_6\text{H}_{12}$ ), retention time 5.482 compound is Cyclohexane ( $\text{C}_7\text{H}_{14}$ ), retention time 5.891 compound is Benzene, 1, 2, 3-trimethyl ( $\text{C}_8\text{H}_{18}$ ), retention time 6.238 compound is Heptane ( $\text{C}_{10}\text{H}_{22}$ ), retention time 6.319 compound is Cyclo propane, (1,2-dimethylpropyl) ( $\text{C}_{11}\text{H}_{24}$ ), retention time 6.524

compound is Undecane, 4, 6-dimethyl- ( $C_{12}H_{26}$ ), retention time 6.609 compound is Heptane, 3, 3, 5-trimethyl- ( $C_{13}H_{28}$ ), retention time 7.665 compound is Cyclohexane, 1, 1, 3, 5-tetramethyl-, trans- ( $C_{14}H_{30}$ ), retention time 7.936 compound is Cyclohexane, 2, 4-diethyl-1-methyl- ( $C_{15}H_{32}$ ), retention time 8.316 compound is 2, 3-Dimethyl-3-heptene, (Z)- ( $C_{16}H_{34}$ ), retention time 9.539 compound

is Cyclohexane, 2, 4-diethyl-1-methyl- ( $C_{21}H_{44}$ ), retention time 9.924 compound is Dodecane, 4, 6-dimethyl- ( $C_{24}H_{50}$ ), retention time 10.956 compound is 2, 3-Dimethyl-3-heptene ( $C_{28}H_{58}$ ), retention time 11.079 compound is Cyclohexane respectively. It was observed from GC/MS analysis; the appeared hydrocarbons are mostly contained gasoline-range products with carbon number of  $C_4$ - $C_{28}$ .

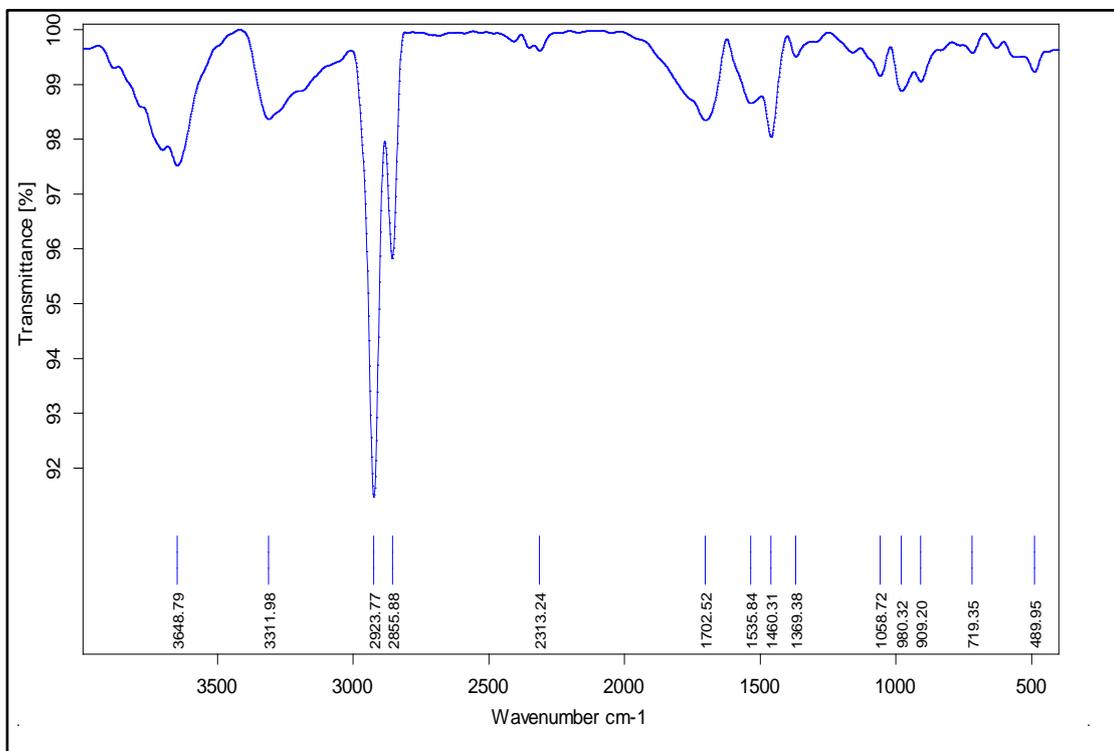


Figure 6. FTIR analyses of the liquid fuel obtained from thermal cracking of waste Glucose bottle

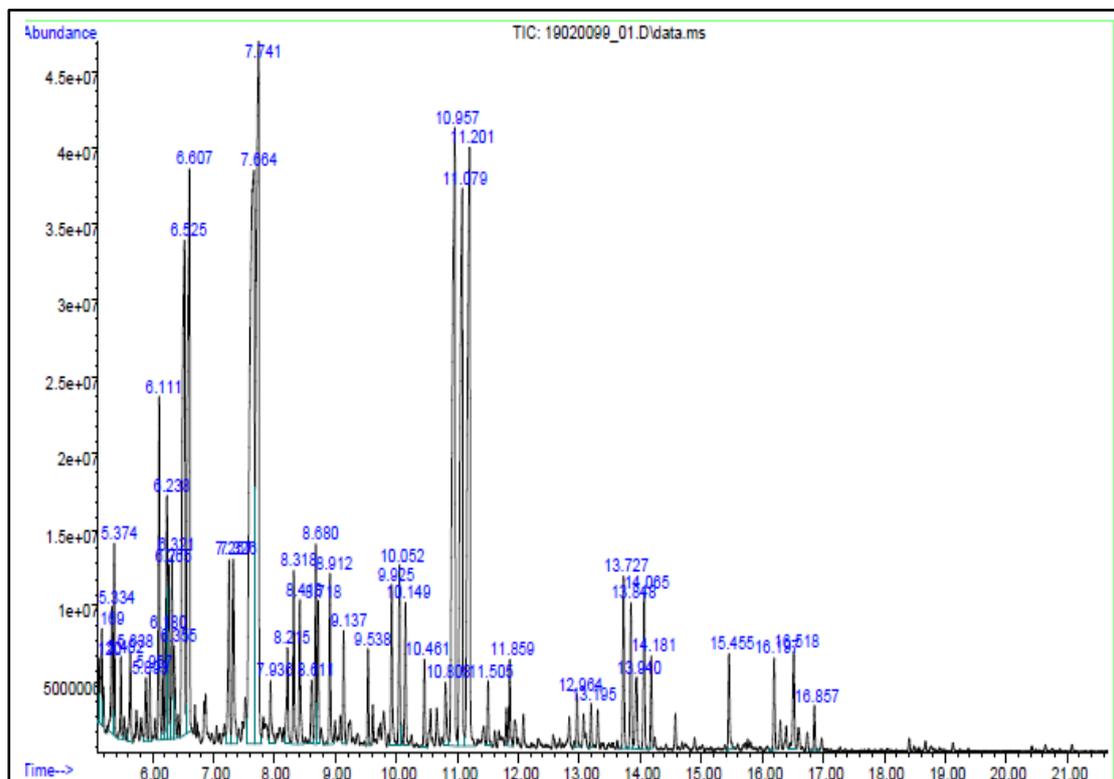


Figure 7. GC/MS analyses of the liquid fuel obtained from thermal cracking of waste Glucose bottle

## 4. Conclusions

1. The thermal cracking of municipal plastic waste (glucose bottle) has been successfully demonstrated in a batch pyrolytic reactor under controlled conditions.
2. The identification test on selected waste plastic was investigated and which showed that the investigated plastic waste belongs to the polypropylene (PP) group plastic.
3. The optimum experimental conditions for the GB thermal cracking were found to be 450°C of temperature and 90 min of reaction time, for maximizing the liquid yield of 72.80%.
4. The GC/MS analysis of the liquid sample indicates that the thermal cracking of waste glucose bottle leads to the production of gasoline range products within the range between C<sub>4</sub>-C<sub>28</sub>. Moreover, the produced liquid fuel appearing in the FTIR spectra consists mainly of aromatic functional groups in -C=C range. Therefore, the produced liquid fuel is termed as aromatic liquid hydrocarbon fuel (ALHF) and it could recommend that the transportation gasoline fuel purposes.

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