

Analysis of Liquid Fuel from Plastic Waste using Refinery Distillation Bubble Cap Plate Column with Integrated Thermal Cracking Method

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Abstract - The objective of this paper is to analyze fuel oil component from thermal cracking pyrolysis with refinery of 4-tray distillation bubble cap plate column. We used a fixed bed type reactor from stainless steel, while the heating process of the electrical reactor reaches a maximum temperature of 750 °C with a heating rate of 15.46 K/min. The process condition used in this research was 500 °C to 650 °C. The results of pyrolysis experiments showed that at 500 to 600 °C and below, the main products of pyrolysis were oily liquids in trays I, II, III and IV or viscous liquids at temperatures above 620 °C in trays I and II and oil fluids in trays III and IV. The obtained liquid fraction of 500-650 °C was analyzed by composition using GC/MS, containing carbon chain C4-C26. FTIR identified fuel in the tray I, at a temperature of 500 and 580 °C, tray II, at 620 °C, tray III, at 600 °C and tray IV, at 650 °C with a dominant functional group composed of alkanes, alkyl aryl ether, primary alcohol, and phenol. The liquid fraction obtained in the case of this study is enriched with naphtha in the range of gasoline and kerosene.

Keywords - Bubble Cap Distillation, FTIR, GC-MS, Plastic waste, Polypropylene, Pyrolysis.

I. INTRODUCTION

Plastic is one commodity that has been so extensively used and sometimes referred to as one of the greatest innovations of the millennium era. The plastic has reached a very wide market due to light-weight, cheap, flexible, reusable, does not rust or rot. Therefore, plastics production has grown up by almost 10% every year on a global basis since 1950 [1]. Used plastics are discharged into environments, then end up in landfills or oceans. Based on data, Indonesia reached the second rank in the world as a plastic waste contributor ending up in the sea reaching 187.2 million tons after China reaching 262.9 million tons [2]; [3]. Piles of plastic waste ending up in the landfill will spend a lot of space because it is difficult to decompose. Last few years the accumulation of excess plastic waste resulted in the emergence of plastic waste disrupting the environment ecosystem. The effects, of plastic waste discharged in the sea, will ruin the ecosystem because animals in the sea will eat it or can reduce the process of photosynthesis in marine plants. In addition, if it burned in settlements or open areas at low temperatures, plastic waste will produce harmful compounds because they can oxidize or react with carcinogenic compounds in the air such as dioxins, nitrogen oxides (NOx), particles and others [4]; [5].

The process of plastic degradation in nature is divided into several categories including physical, biological, and chemical processes. Physical degradation processes in nature occur through pressure, humidity and heat from the sun. Based on its chemical compounds, plastic is composed of hydrocarbon chain polymers derived from petroleum refining. The bonds between the hydrocarbon monomers are very strong and make it difficult in degradation process at

ambient temperature (32 °C), so it is very difficult to be biologically degraded by enzymes and bacteria and takes a very long time for the degradation process [6]. It is recommended that an energy recovery is a good option for plastic waste treatment and the fact that there is a limited need for pre-treatment when dealing with mixed and contaminated plastics [7]; [8]. In addition, an increased demand for plastics causes petroleum depletion as fuel from non-renewable fossils due to petroleum-based plastic raw materials. Therefore, the recycling method is effectively and economically processed by pyrolysis method as it can restore the energy contained in the plastic waste.

Thermal cracking or pyrolysis is a decomposition process of long-chain hydrocarbon (polymer) by heat in the absence of oxygen to produce short chain organic molecules and several carbons as residues and volatile hydrocarbons which can be condensed as fuel oil and non-condensed as fuel gaseous [9]. This is quite important from the energy, environmental, and economic point of view. This process takes place at high temperatures following the mechanism of free radical reactions [10]; [11]. This reaction is an initial stage in which the weak bonds chain is broken due to rising temperatures, followed by the formation of free radical propagation stage, then these free radicals will split again to form new smaller free radicals, which results in a stable compound. At certain temperatures, R* is not stable so it will be broke again at the stopping stage. The presence of free radicals will form stable compounds, that produce hydrocarbon compounds in form of paraffin, isoparaffin, olefins, naphthenes and aromatics, and the gas non-condensable gas [12].

There are four types of decomposition reaction mechanism of plastics depending on the plastic types:

1. End-chain scission, in which; the polymer is broken up from the end groups successively yielding the corresponding monomers. When this polymer degrades by depolymerization, the molecules undergo scission to produce unsaturated small molecules (monomers) and another terminal free radicals.

2. Random-chain scission, in which; the polymer is broken up randomly into smaller molecules of varying chain lengths, producing a volatile with or without double bonds.

3.Chain-stripping, in which; the reactive substituents or side groups on the polymer chain are eliminated, leaving an unsaturated chain. This polyene then undergoes further reaction, including β -scission, aromatization, and coke formation.

4. Cross-linking, in which; the formation of a chain network occur from thermosetting polymers when heated at high temperature. This is pyrolytic condensation and rearrangement of carbon networks to form high-strength materials.

These different mechanisms are related to the bond dissociation energies, the chain defects of the polymers, the aromatic degree and the presence of halogen and other hetero-atoms in the polymer chains. The liquid fuel obtained from the pyrolysis proceeded by purification process cannot be directly used as fuel, because it has not fulfilled liquid fuel characteristics, and the presence of impurities (ash) from the feedstock [13]; [14]. Therefore, in this study

purification of pyrolysis products was conducted using Distillation Bubble Cap Tray Column. The complex pyrolysis products may also be grouped as petroleum gases, gasoline, kerosene, diesel, and wax. The above fuels contain hydrocarbon group with different carbon chain lengths as given in Table I.

TABLE I. HYDROCARBON RANGE IN COMMERCIAL FUELS [13]

Fuels	LPG	Gasoline	Kerosene	Diesel	Heavy Fuel Oil
HC	C ₃ to C ₄	C ₄ to C ₁₂	C ₁₂ to C ₁₅	C ₁₂ to C ₂₄	C ₁₂ to C ₇₀

II. MATERIALS AND METHODS

A. Materials

Samples were sorted out according to resin codes developed by the Society of Plastic Industries. Raw materials used in this study derived from Polypropylene (PP) type plastic ($\rho = 1.30-1.58$ g/cc; TM = 168-175 °C [14] such as drink plastic waste. that was obtained from scavengers around Keputih Sukolilo Surabaya, Indonesia. The plastic waste was washed to separate the dirt and then, it was cut into small pieces, with sizes of 1 x 3 cm by using enumerator machines, to minimize the volume of the sample chamber in the reactor.

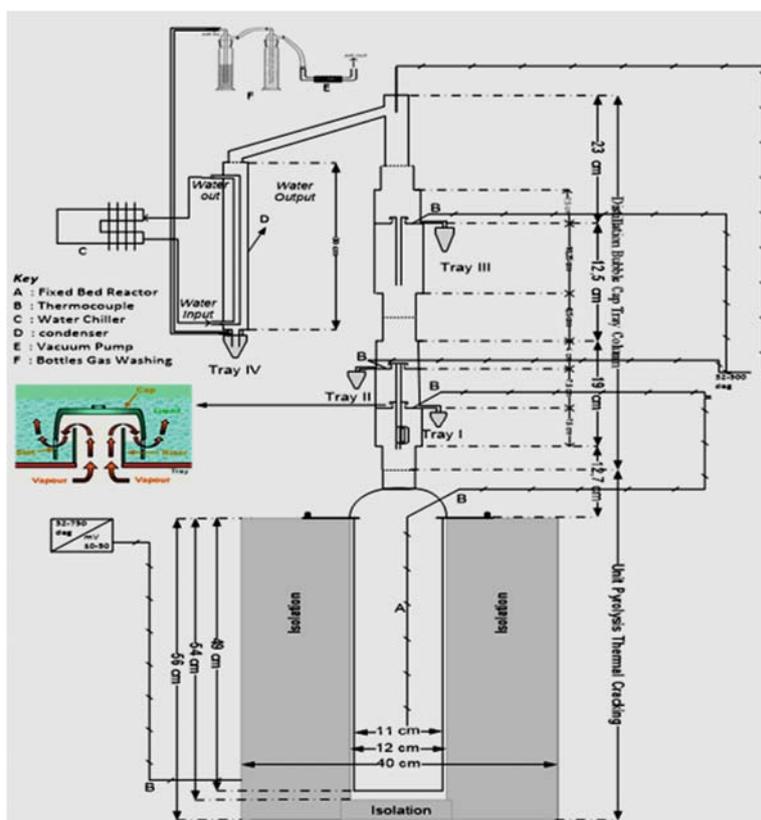


Fig. 1. Schematic of thermal cracking pyrolysis circuit integrated with distillation bubble cap column.

B. Experimental Setup

The prepared sample was weighed as much as 500 g filled into the pyrolysis reactor unit. This study used a fixed bed type reactor from stainless steel while the glass distillation cap column was in a semi-batch process condition. The reactor heating process electrically reaches a maximum temperature of 750°C. The temperature was measured in the furnace using Integral Proposal (PI) method with Off-Set 2 °C as process variable controller. The heating rate is 15.46 K / min, including the slow pyrolysis category. Process conditions at temperatures of 500, 520, 540, 560, 580, 600, 620 and 650 °C under vacuum conditions ($\Delta P_{input} = -10\text{mmH}_2\text{O}$; $\Delta P_{out} = -7 \text{ mmH}_2\text{O}$) to remove air (oxygen) in the reactor. The steam coming out of the reactor was measured at a temperature using a Leybold series 666 209 digital thermocouples, before passing through the distillation bubble cap column. Distillation product bubble cap column consists of four trays. Tray I = the heaviest fractional having the highest boiling point, Tray II = fractional distillation had lower boiling point than tray I, Tray III = fractional distillation had lower boiling point than tray II. Separation of these three trays by releasing latent heat to obtain oil fuel condensate, while the tray IV is the

lightest tray condensed with condensers to obtain condensate. Each tray was equipped with a Leybold series 666 209 thermocouple, while a non-condensable vapor would go through the solvent solution to dissolve the volatile compound through Bottles Gas Washing so as not to be wasted into the atmosphere. The condensate of each tray was accommodated for each process temperature, to analyze the fuel characteristics produced.

III. RESULTS AND DISCUSSION

A. Effect of Temperature on Chemical Composition Using Fourier Transform Infrared (FTIR) Spectroscopy:

The FTIR spectra of all pyrolysis products produced through distillation bubble cap plate column. at different process conditions are represented in Fig.2. Functional groups of the constituents of samples could be observed by characteristics absorption bonds of each group of atoms through the infrared spectra. FT-IR analysis was carried out in the range of 400-4,000 cm^{-1} with sensitivity of 50. The spectrum region and intensity of each bond is presented in Table II.

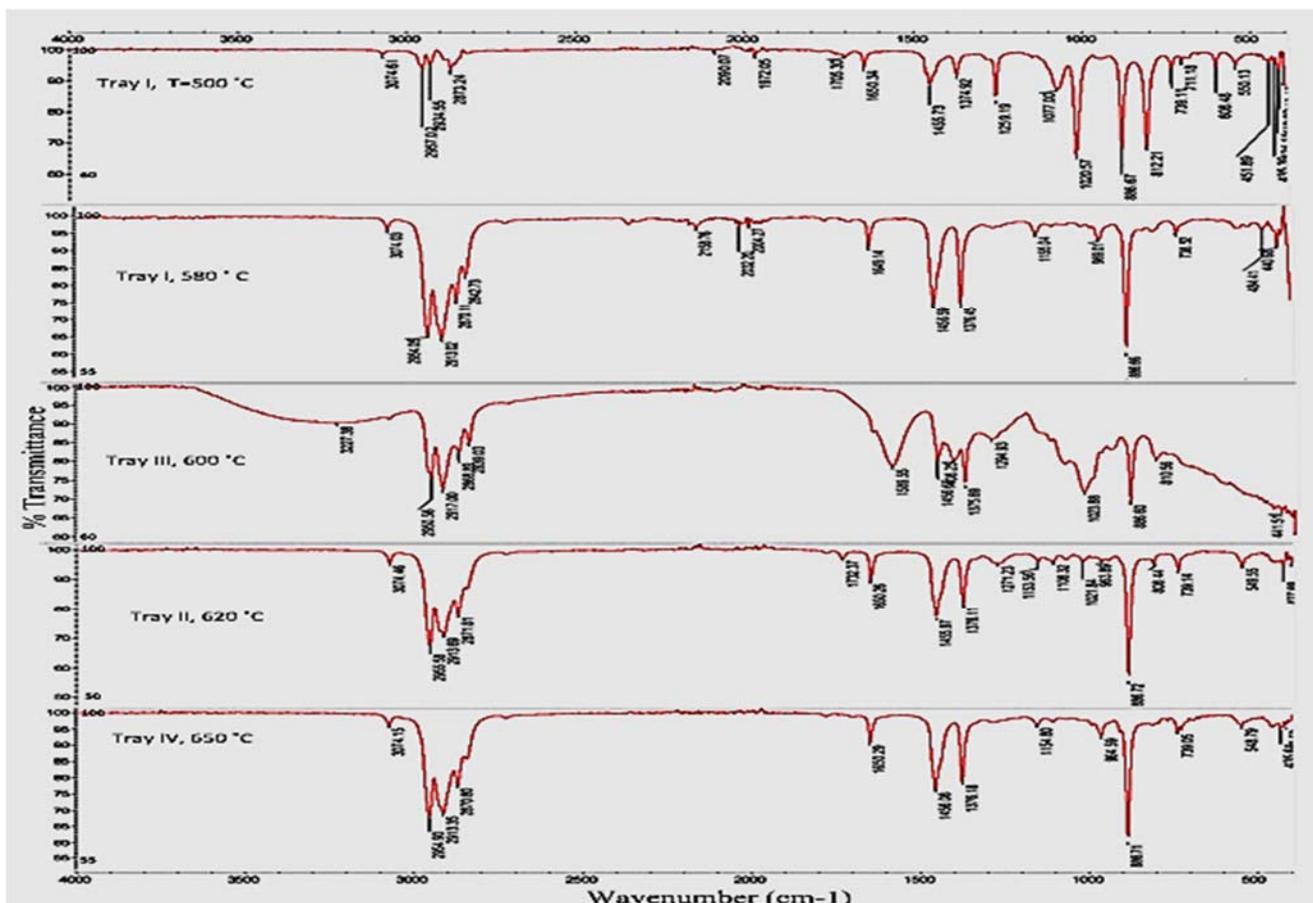


Fig. 2. FTIR analysis of distillation result Bubble Cap Tray Column polypropylene plastic waste fuel oil

TABLE II. FREQUENCY RANGE OR FUNCTIONAL GROUP (CM-1) AND REGION SPECTRUM [15] AND RESULT OF FTIR PYROLYSIS PRODUCT THERMAL CRACKING OF POLYPROPYLENE PLASTIC WASTE

Wavenumber or peaks (cm ⁻¹)	500 °C	580 °C	620 °C	600 °C	650 °C	Range Peaks (cm ⁻¹)	Possible Functional Group	Functional Group
	Tray I	Tray I	Tray II	Tray III	Tray IV			
711-739	√	√	x	√	√	880-700	C-H	alkene, 1,3-disubstituted
810-886	√	√	√	√	√	810 ± 20	C-H	alkene, 1,2,3,4-tetrasubstituted
964-969	x	√	x	√	√	980-960	C=C	alkene, disubstituted (trans)
1020-1023	√	x	√	x	x	1075-1020	C-O	alkyl aryl ether
1077	√	x	x	x	x	1085-1050	C-O	primary alcohol
1155-1154	x	√	x	√	√	1150-1085	C-O	aliphatic ether
1374-1376	√	√	√	√	√	1390-1310	O-H	phenol
1408	x	x	√	x	x	1440-1395	O-H	carboxylic acid
1455-1456	√	√	x	√	√	1450-1465	C-H	alkane, methyl group
1589	x	x	√	x	x	1650-1580	N-H	amine
1650	√	√	x	√	√	1650-1600	C=C	conjugated alkene
1705	√	x	x	x	x	1710-1680	C=O	conjugated acid
1972	√	x	x	x	x	2000-1900	C=C=C	allene
2004-2090	√	√	x	x	x	2140-1990	N=C=S	isothiocyanate
2842-2913	√	√	√	√	√	3000-2840	C-H	alkane
3074	√	√	x	√	√	3100-3000	C-H	alkane
3227	x	x	√	x	x	3333-3267	O-H	alcohol

TABLE III. THE MAIN COMPONENT FUEL LIQUID OF FTIR ANALYSIS RESULTS

Compound Name	Spectrum Region					Indeks
	Tray I	Tray I	Tray II	Tray III	Tray IV	
Hexamethylcyclotrisiloxane, 98%	√	x	x	x	x	16889
trans-2,3-Epoxybutane, 96%	√	x	x	x	x	1406
2-Methyl-1-heptene, 99%	√	√	x	√	√	143
2-Methyl-1-hexene, 96%	√	√	x	√	√	141
(R)-(+)-Limonene, 97%	√	x	x	x	x	51
2-Methyl-1-pentene, 99%	√	√	x	√	√	137
2-Ethyl-1-hexene	√	√	x	√	√	142
2-Methyl-1-pentene	√	√	x	√	√	136
2-Methyl-1-butene	√	x	x	x	x	133
Poly(Propylene), Syndiotactic	x	√	x	x	x	38
Poly(Propylene), Atactic	x	√	√	x	x	41
2-Methyl-1-undecene, 98%	x	√	x	√	√	144
Poly(isoprene), 53% 3,4 + 29% 1,2	x	√	x	√	√	623
2,3-Dimethyl-1-butene, 97%	x	√	x	√	√	135
2,4-Dimethyl-1-pentene, 97%	x	x	x	√	√	138
DL-limonene, tech., 75%	x	x	x	√	√	282
Polypropylene + poly(ethylene:propylene)	x	x	√	x	x	324
Polypropylene, isotactic, average MW ca. 250,000	x	x	√	x	x	17997
Polypropylene	x	x	√	x	x	737
Polypropylene + 20% talcum	x	x	√	x	x	303
Polypropylene, atactic	x	x	√	x	x	565
Polypropylene, isotactic	x	x	√	x	x	942
Poly(propylene:ethylene), 83 mol% C3	x	x	√	x	x	499
Polypropylene+poly(ethylene:propylene)	x	x	√	x	x	624
Poly(propylene:butenone), 2:1	x	x	√	x	x	1061

The FTIR spectrum of condensate in tray I showed at 500 °C and 580 °C, tray II at 620 °C, tray III at 600 °C and tray IV at 650 °C indicated the presence of more functional groups of paraffin (alkane), olefin (alkene) and aromatic groups in the form of 2-Methyl-1-heptene, 2-Methyl-1-hexene, 2-Methyl-1-pentene, 2-Ethyl-1-hexene, 2-Methyl-1-pentene, 2-Methyl-1-butene compound, because of this condensate generated potentially used as alternative fuel. Whereas, in tray II at temperature 620 °C showed functional groups dominant alkene, alkyl aryl ether, nitro compound, carboxylic acid and alcohol in the form of Polypropylene, Poly (propylene: ethylene) and Poly (propylene: butanone). To be used as fuel, polymers must go through a thermal cracking process to break polymer bonds into monomers. The same functional group results were also obtained [16]; [17] but they used fractional distillation.

B. Effect of Temperature on Chemical Composition Analyzed by GC-MS

GC-MS can provide qualitative and quantitative data of compounds that are components of fuel oil from plastic pyrolysis because the area under curve (AUC) shown on the chromatogram is directly proportional to the concentration

of each component present in the sample. Gas chromatographic analysis will get the possibility of the number of fuel oil components and their respective compositions. While to determine the type of fuel oil component was analyzed by GC, hereinafter MS further identify with spectra derived from NIST and WILEY. The analysis with GC-MS was performed by injecting the distillate of the pyrolysis product into the column. The trailer vapor then carried by the carrier gas into the column. The column would separate the components of the fuel oil so that it could be detected by the detector and produced a chromatogram. The analysis of fuel compound content in this study was performed with mass spectrum analysis based on "peak base" and index of similarity (SI) by comparing NIST spectral 62 and Wiley 299.LIB. The base peak was the largest peak in the spectrum and rated 100%. If the SI value was close to 100% then the compound detected has similarities with the comparison data. The oil composition was been evaluated by the SHIMADZU GC-MS-QP2010S tool producing 50 peak chromatograms. As shown in Figure 3. There are 50 peaks that appear every pyrolysis process, selected 10 main peaks which have the highest % area. As shown in Tables IV to VIII.

TABLE IV. MAIN COMPONENT GC-MS TRAY I TEMPERATURE PROCESS AT 500°C

Peak #	Name Of Compound	Molecular Formula	Mol weight	components, (% Area)
1	2,4-Dimethyl-1-heptene	C9H18	126	42.11
2	1-Decene, 2,4-dimethyl	C12H24	168	15.46
3	1-Undecene, 7-methyl	C12 H24	168	9.57
4	Cyclotrisiloxane	C6 H18 O3 Si3	222	3.06
5	Cyclohexane, 1,3,5-trimethyl	C9H18	126	4.06
6	Decane, 4-methyl	C11H24	156	5.28
7	Heptane, 4-methyl	C8H18	114	2.79
8	2-Hexene, 4,4,5-trimethyl	C9H18	126	1.42
9	Cyclopentasiloxane, decamethyl	C10 H30 O5 Si5	370	0.82
10	2-Hexene, 4,4,5-trimethyl	C9H18	126	0.74

TABLE V. MAIN COMPONENT GC-MS TRAY I TEMPERATURE PROCESS AT 580°C

Peak #	Name Of Compound	Molecular Formula	Mol weight	components, (% Area)
1	1-Undecene, 7-methyl	C12 H24	168	21.93
2	2,4-Dimethyl-1-heptene	C9H18	126	17.47
3	1-Heptacosanol	C27H56O	396	4.15
4	1-Dodecene	C12H24	168	4.07
5	1-Decene, 2,4-dimethyl	C12 H24	168	3.64
6	2-Hexyl-1-octanol	C14H30O	214	3.47
7	1-Heptacosanol	C27H56O	396	3.4
8	2-Hexyl-1-octanol	C14H30O	214	2.56
9	Cyclododecanemethanol	C13H26O	198	2.18
10	2-Hexyl-1-octanol	C14H30O	214	2.17

TABLE VI. MAIN COMPONENT GC-MS TRAY III TEMPERATURE PROCESS AT 600°C

Peak #	Name Of Compound	Molecular Formula	Mol weight	components, (% Area)
1	1-Octene, 3-ethyl	C10H20	140	61.07
2	Heptane, 4-methyl	C8H18	114	9.21
3	1-Pentene, 2-methyl	C6H12	84	3.86
4	1-Octene, 3,4-dimethyl	C10H20	140	2.29
5	Cyclohexane	C9H18	126	2.23
6	Propane, 2-methyl	C4 H10	58	2.01
7	Cyclopentane, 1,1,3,4-tetramethyl	C9H18	126	1.59
8	2-Hexene, 3,5-dimethyl	C8 H16	112	1.47
9	1,4-Pentadiene, 2,3,4-trimethyl	C8 H14	110	1.12
10	2,4-Dimethyl 1,4-pentadiene	C7H12	96	1.07

TABLE VII. MAIN COMPONENT GC-MS TRAY II TEMPERATURE PROCESS AT 620°C

Peak#	Name Of Compound	Molecular Formula	Mol weight	components, (% Area)
1	2,4-Dimethyl-1-heptene	C9H18	126	25.97
2	1-Undecane, 7-methyl	C12 H24	168	16.79
3	1-Octanol, 3,7-dimethyl	C10H22O	158	8.95
4	1-Undecane, 7-methyl	C12H24	168	4.69
5	2-Hexyl-1-octanol	C14H30O	214	4.18
6	Acetone	C3H6O	58	3.15
7	1-Decanol, 2-hexyl	C16H34O	242	3.01
8	1-Heptacosanol	C27 H56 O	396	2.53
9	Heptane, 4-methyl	C8H18	114	1.6
10	Cyclohexane, 1,3,5-trimethyl	C9H18	126	1.57

TABLE VIII. MAIN COMPONENT GC-MS TRAY IV TEMPERATURE PROCESS AT 650°C

No.	Senyawa yang diduga (Nama Komponen)	Rumus Kimia	Berat Molekul	Komponen (% Area)
1	2,4-Dimethyl-1-heptene	C9H18	126	40.74
2	1-Undecane, 7-methyl	C12 H24	168	4.19
3	2-Undecane, 4,5-dimethyl	C13H26	182	4.08
4	1-Decane, 2,4-dimethyl	C12 H24	168	3.32
5	1-Undecane, 7-methyl	C12 H24	168	3.24
6	1-Pentene, 2-methyl	C6H12	84	3.2
7	Heptane, 4-methyl	C8H18	114	2.95
8	3-Undecane	C11H22	154	2.11
9	Acetone	C3H6O	58	2.08
10	1-Octene, 3,4-dimethyl	C10H20	140	1.76

As can be seen in Tables IV to VIII, the components in pyrolysis oils are grouped into categories of paraffin, olefin, aromatic, cyclic, and oxygen compounds which are the main components of the fuel. Thus, the pyrolysis product from polypropylene plastic waste can be used as fuel gasoline, kerosene or diesel by purification using Distillation Bubble Cap Plate Column.

IV. CONCLUSION

FTIR and GC-MS results showed that the liquid product consisted of a wide spectrum of hydrocarbons mainly distributed within the C4–C27 carbon number

range. The liquid fraction obtained in case of the distillation bubble cap plate column was enriched in the naphtha range hydrocarbons with a preponderance in gasoline range hydrocarbons.

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