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Degradation of Plastic Wastes (PP, PET, and LDPE) for Liquid Fuel Production as alternative energy by Using Vacuum Pyrolysis Method.

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ABSTRACT

The plastic wastes are the more available material in the environment. These material types are: PolyPropylene (PP),PolyEthylene Terephthalate(PET) and Low Density Poly Ethylene(LDPE). Thermal degradation of those three materials was studied under vacuum environment individually and as a combination of all. The output products were characterized by Gas Chromatography(GC) and Fourier Transform Infra-Red(FTIR). Some of the physical properties was measured such as density, boiling point. The results show that degradation of combined materials was produced liquid fuel compared with standard properties preferable than individual once. A mixture product of same carbonyl compounds such carboxylic acid and unsaturated aldehyde was preliminary characterized.

Introduction.

In many countries both energy systems and waste management systems are currently undergoing changes. One driving force for these changes is the threat of global climate change caused by increasing concentrations of carbon dioxide (CO2), methane (CH4) and other greenhouse gases. This threat has lead the global society to sign the Kyoto protocol 1997 which simplistically states that the developed countries should reduce their emissions by 5 % until the year 2010 compared to 1990. [1]

Alternative fuels developed from a reliable domestic source have the potential to overcome many economic and environmental problems, by providing a steady, low cost source of fuel, by providing local employment in energy production, and by providing fuel types that are clear. The percentile contributions from current major alternative/ renewable sources are as follows: (a) biomass 53%, (b) hydropower 36%, (c) geothermal 5%, (d) wind 5%, and (e) solar 1% . [2]

But economic growth and changing consumption and production patterns are resulting into rapid increase in generation of waste plastics in the world. In Asia and the Pacific, as well as many other developing regions, plastic consumption has increased much more than the world average due to rapid urbanization and economic development.

The world's annual consumption of plastic materials has increased from around 5 million tones in the 1950s to nearly 100 million tones; thus, 20 times more plastic is produced today than 50 years ago. This implies that on the one hand, more resources are being used to meet the increased demand of plastic, and on

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the other hand, more plastic waste is being generated. Due to the increase in generation, waste plastics are becoming a major stream in solid waste. After food waste and paper waste, plastic waste is the major constitute of municipal and industrial waste in cities. Even the cities with low economic growth have started producing more plastic waste due to plastic packaging, plastic shopping bags, PET bottles and other goods/appliances using plastic as the major component [3]

For worldwide cultivation purposes farmers use numerous plastics. They use polyethylene poly bags or polyethylene sheets. Polyethylene poly bags parts and polyethylene sheets are used to protect crops from adverse situation such as natural disaster, muddy water and some external parasites insects. After that, the used plastics become a waste and they are non-biodegradable. Most common way to deal with those agricultural waste plastics is landfill/incineration. However this method is not a sustainable solution in the long run, because it will create ecological problems. So the problems of waste agriculture plastics cannot be solved by landfill/incineration. Because safe depots are expensive and incineration stimulates the growing emission of harmful green house gases for example, NOx, SOx, COx etc.; Natural State Research, Inc.

(NSR) can resolve the problems of agricultural waste plastics by converting it into high energy liquid hydrocarbon fuel. Produced fuel can be use alternative of gasoline, diesel, heating oil and aviation fuel. To mitigate the present market demand we can substitute the method as a potential source of energy .[4] The only sustainable solution is degradation of polymer into various smaller molecular weight fragments. [5]

As landfill and incineration become more expensive and less accepted, the recycling of plastic wastes is gaining increasing importance. More emphasis is thus being given to new disposal options, which have high energy recovery values and are more environmentally attractive.

Pyrolysis is one promising method for the treatment of mixed and contaminated plastic wastes. Plastics are thermally degraded to produce useful liquid hydrocarbons, which can then either be added to existing fuel or solvent product, or returned to a refinery where they can be added to the feedstocks. Results of pyrolysis tests showed that pure samples of polyolefinic and polystyrene resin can readily be pyrolysed to produce liquid yields in excess of 70%. However, liquid yields were affected by heating rates and heat loss patterns in the reactor system. Further experimental work suggests that when pyrolysed, mixed plastic wastes behave much like the resins from which they originate. [6]

The aim of this work is to degradation of plastic wastes under vacuum pyrolysis in order to convert plastic wastes into useful materials such as transport fuel, petrochemical industries materials and reduce the dependence on fossil fuel, in other hand minimize the environmental pollution. Pyrolysis of PP, PET and LDPE those a good processes in ecofriendly methods to get rid of wastes and it is better than incineration and landfilling processes.

Experimental.

Fig(1) show the experimental apparatus for degradation of plastic waste consist of a batch reactor made of stainsteel (5.5D × 11H) cm in which the reaction takes place; heated by a heating oven with a temperature controller contacted to Flask three neck for waxes, heating by heat mantle and contacted to condenser and three necked flask for liquid product, . Prior to the reaction vacuum was created in the reactor to ensure that no oxygen is left there. Polymer was charged into the reactor at the beginning and the reactor was heated up.

A constant time for one batch was used throughout the 2.5 hour. in first 5 min; a linear temperature increase was observed and then increased with slow rate for remaining 10 minutes inter heating oven and 25 minutes inter reactor .

The process uses thermal degradation to heat the waste plastic to form liquid slurry in the absence of atmospheric oxygen at a temperature ranging from 370 – 420 C0 without catalyst and using the waste plastic of plastic shopping bags type (LDPE), vegetable boxes type (PP) and distilling water bottles type(PET).

These plastic types were investigated individually and in combination with each other. In a laboratory scale, the weight of a single batch of input plastic for the fuel production process 50 grams for one type. The waste plastics are collected, optionally sorted, cleaned of contamination and grinded into small pieces prior to the thermal liquefaction process.

The end products consist of liquid products were collected through the condenser in a collecting vessel kept in cooling and gases will be captured in plastic tire and the solid residue (waxes, coal) are kept . And then various tests have been performed to investigate the compositions of producer fuel. FTIR analysis , (GC) ,density and boiling point measurements and some physical properties.

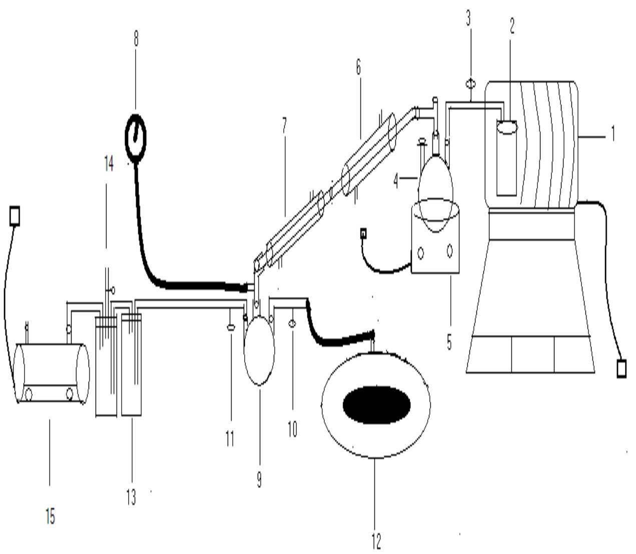


Figure 1: Schematic diagram of the degradation of waste plastics ; (1-heating oven; 2-reactor; 3-control valve; 4- Flask three necks for wax; 5- Mantle Heater; 6- Condenser (1); 7- Condenser (2); 8- vacuum gauge; 9-- Flask three necks for liquid; 10- gases control valve; 11- vacuum control valve; 12- Rubber tire for gas reservoir; 13- trap; 14-vacuum valve; 15- vacuum pump).

Experimental calculation.

The conversions to volatile products were calculated as the fraction of initial mass of polymer reacted to form the volatile products. The yield of liquid product was calculated as the mass of liquid collected divided by the mass of the initial amount of polymer and represents the fraction of original polymer converted to liquid products.

The yield of gas product was calculated as the mass of gas collected divided by the mass of the initial amount of polymer. The coke yield was calculated by dividing the mass of nonvolatile polymer in the reactor by original mass of polymer.

Results and discussion.

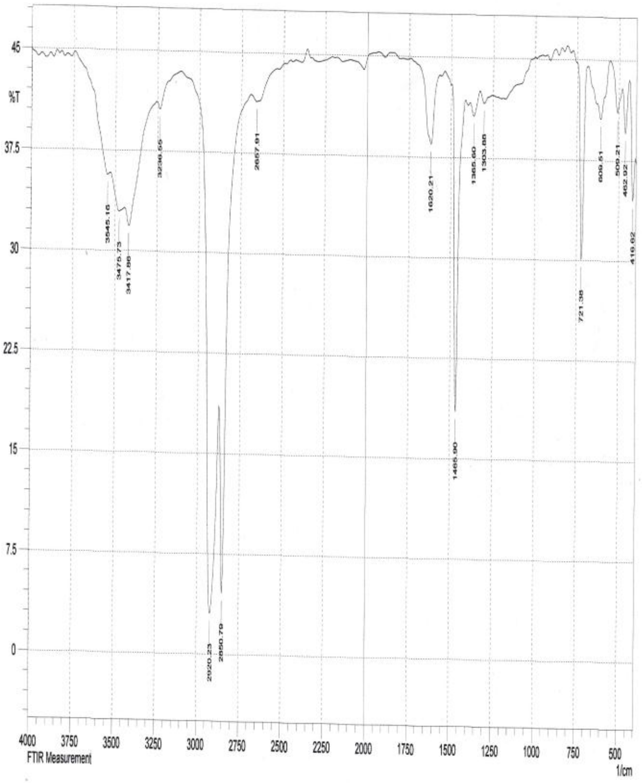
FTIR Analysis :

The three different products (PP, PE, PET) were characterized by (FTIR- model: Bruker- Aleha: Germany), goes to experimental part. Tables 5 and Fig 2- 4 Shows waves lengths of functional groups of PE, PP and PET .

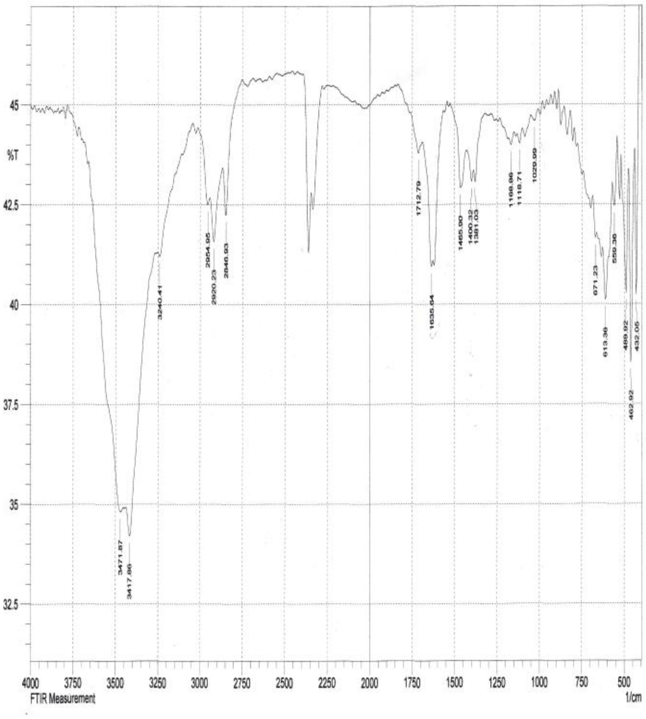
Fig (5-7) show functional groups of N-H stretch ,=C-H stretch for alkene , C-H stretch so for alkene and alkane ,C=C stretch and C-H scissor for alkene ,C-H methyl rock, =C-H bend for alkene . [7]

Fig (8-10) shows functional groups of N-H stretch, =C-H stretch for alkene , C-H stretch so for alkene and alkane ,C=C stretch and C-H scissor for alkene ,C-H methyl rock, =C-H bend for alkene additional to showing new functional groups, C-H stretch for aldehyde ,C=O stretch for unsaturated aldehyde and C-O stretch so for aldehyde .

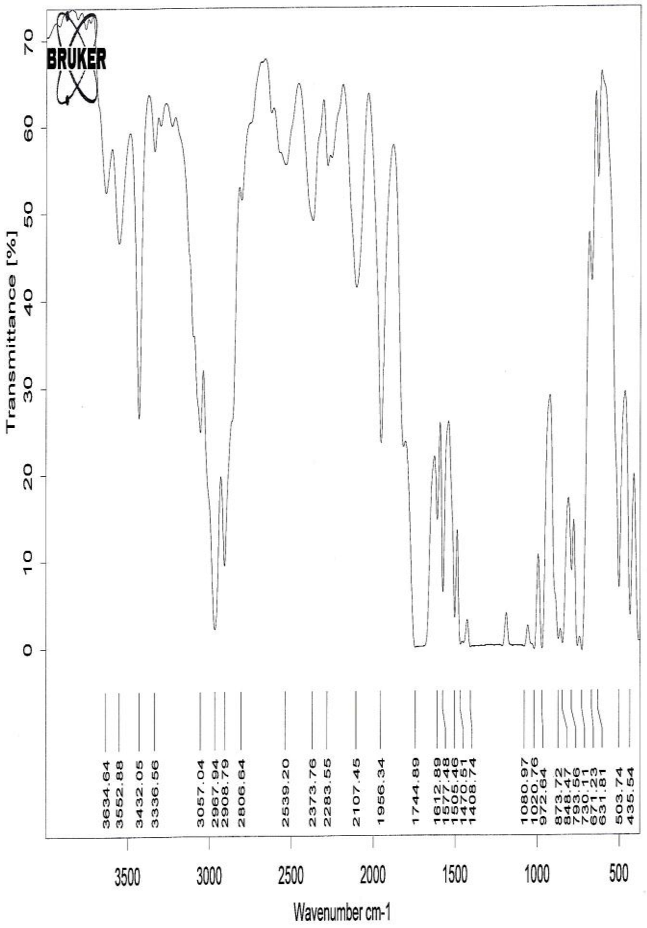
Fig (11) shows functional groups (O-H) of carboxylic acid, =C-H stretch for aromatic, C=O stretch for carboxylic acid, C=C stretch for aromatic, (C-C) stretch in the ring and C-O stretch so for carboxylic acid. Fig (12) appear functional groups of (O-H), =C-H, C-H, C=O, C=C ,(C-C) in the ring and C-O stretch for mixture of carbonyl compounds .[8]



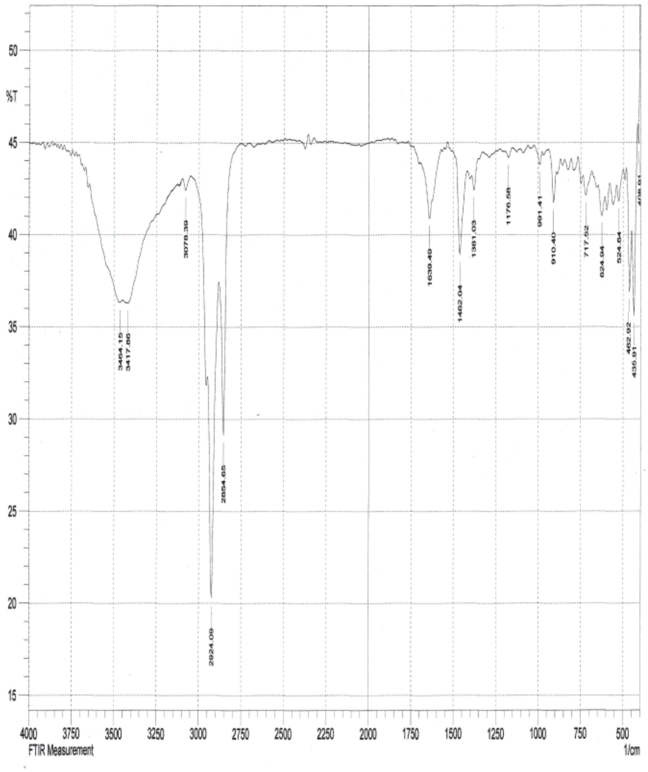
Figure(٢):FTIR for LDPE(plastic shopping bags).



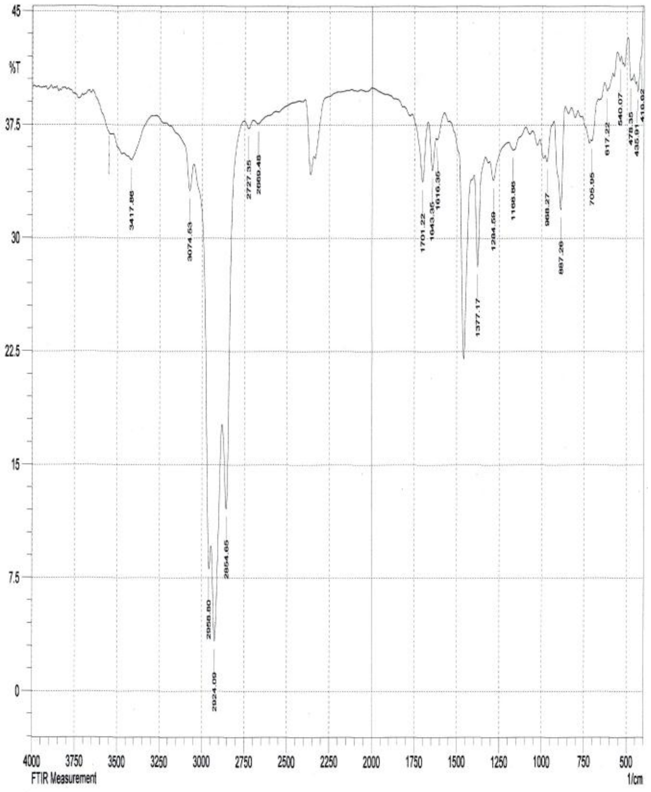
Figure(٣):FTIR PP(plastic vegetable boxes).



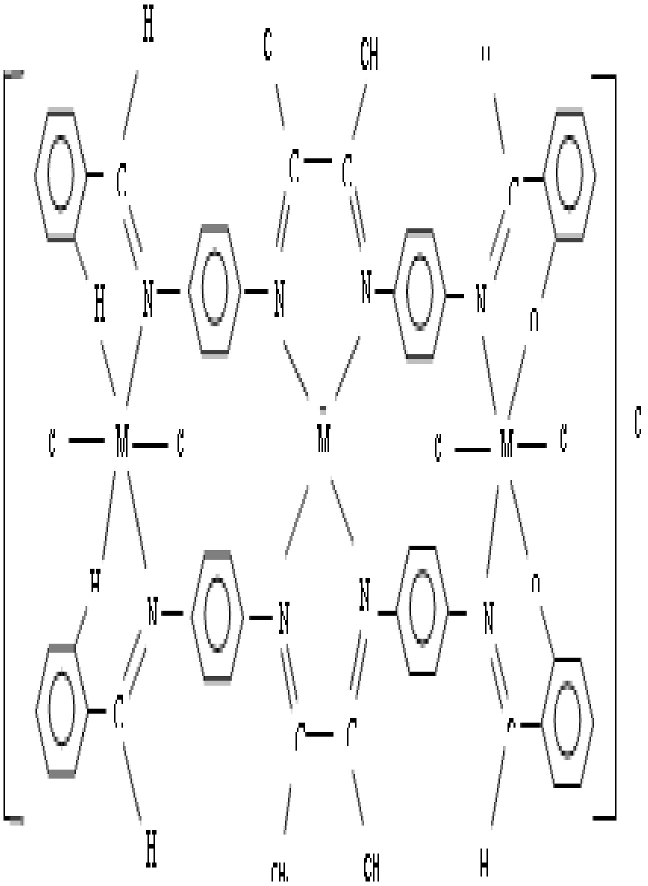
Figure(٤):FTIR for PET (water bottles).



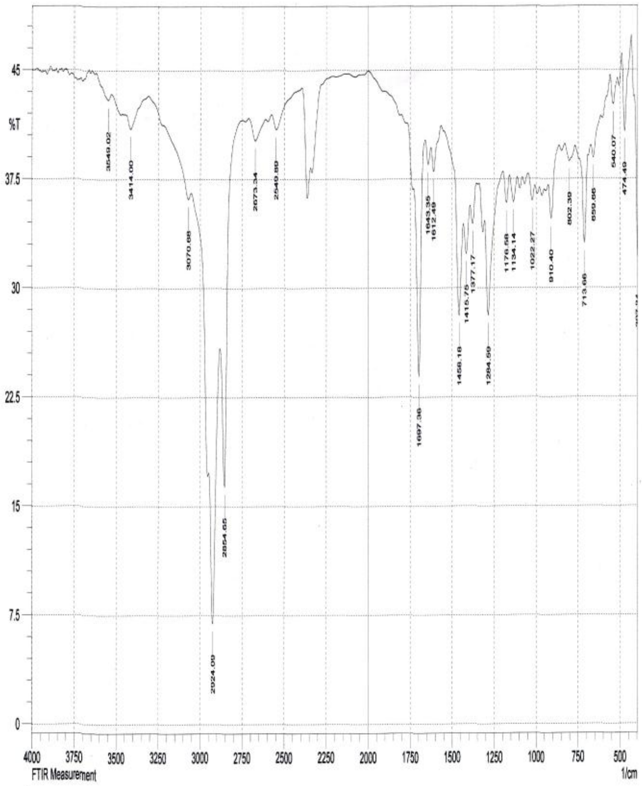
Figure(٥):FTIR for liquid product of (PE).



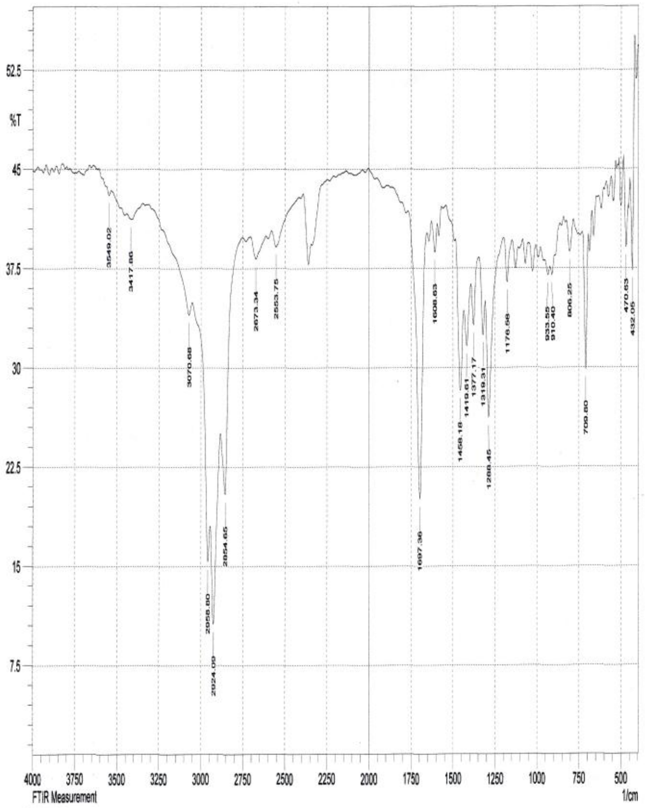
Figure(٦):FTIR for liquid product of (PP)



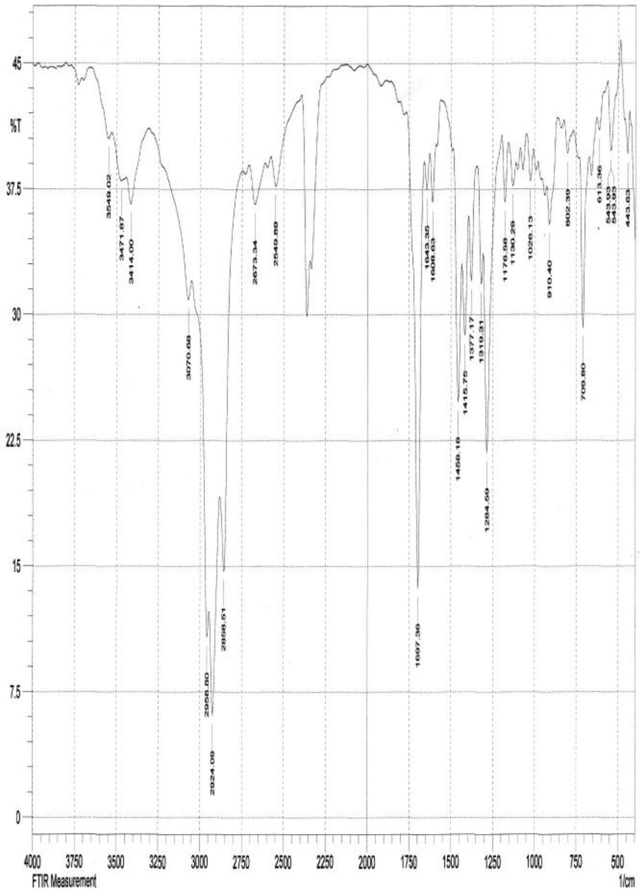
Figure(٧):FTIR for liquid product of (PE and PP).



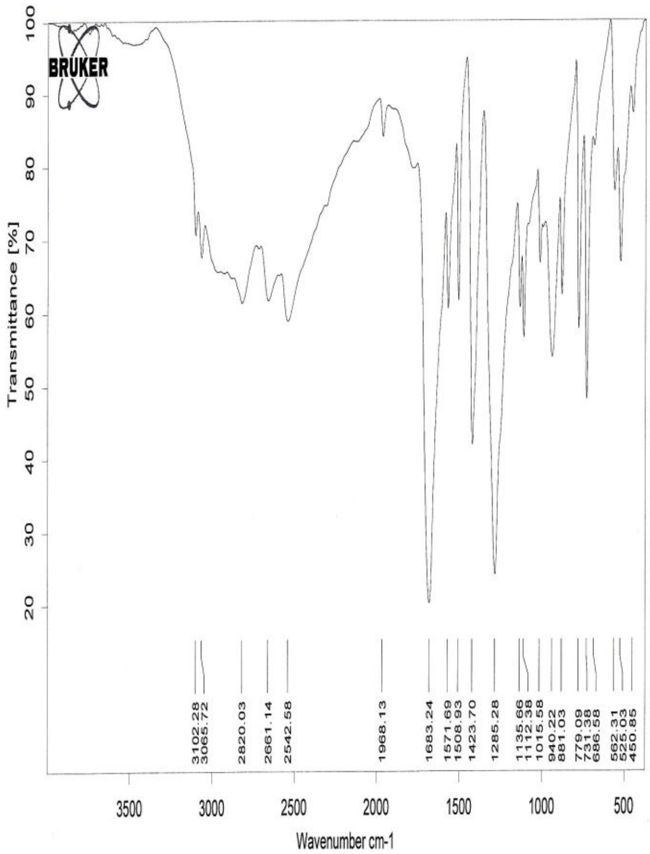
Figure(٨):FTIR for liquid product of (PE and PET).



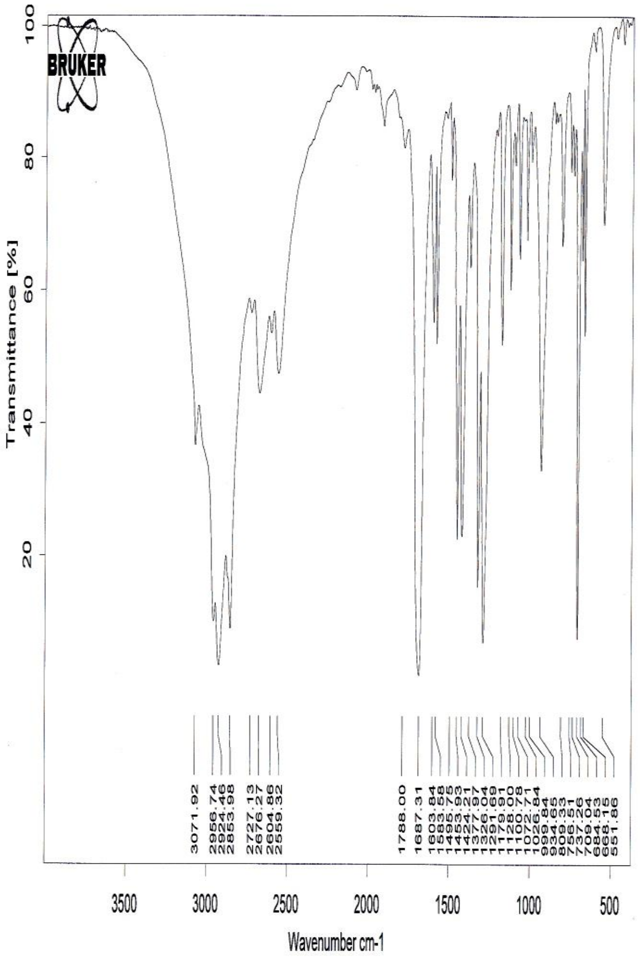
Figure(١٠):FTIR for liquid product of (PE , PP and PET).



Figure(٩):FTIR for liquid product of (PP and PET).



Figure(١١):FTIR for terphethalic acid.



Figure(1٢):FTIR for mixture of carbonyl compounds(Milky wax) .

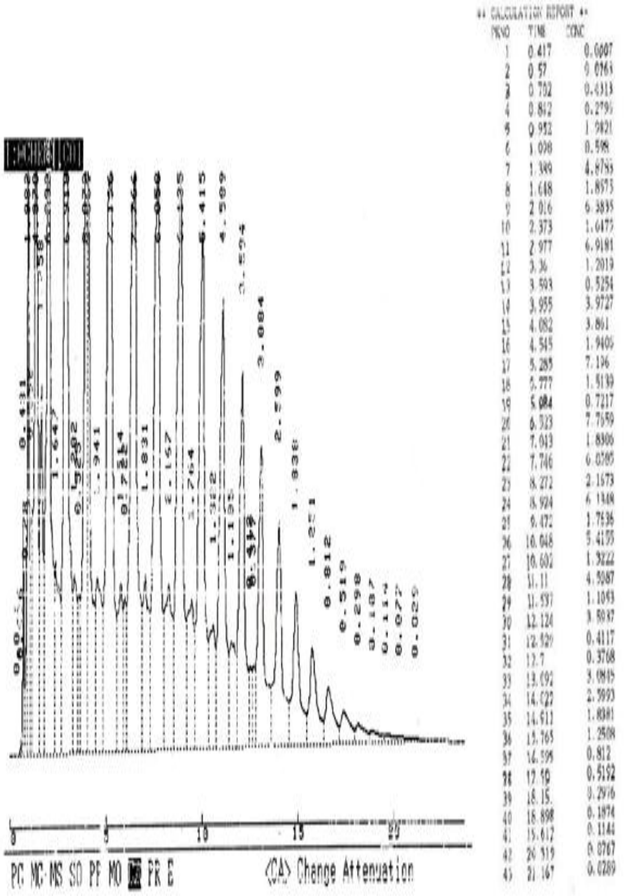
Table 5:FTIR characteristic absorption bands for liquid products.

Plastic wastes	PE	PP	Terphatha-lic acid	mixture of carbonyl compound	PE+PET+ PP	PP+ PET	PE+PET	PE+PP	PET
υ(N-H)	3464, 3417	3464, 3417	---	---	3549,3471,3417	3549,3471,3414	3549,3471,3414	3552,3479,3417	3552, 3432
υ(O-H) carboxylic acid	---	---	3102	associ-ating	---	---	---	---	---
υ(=C-H) alkene, aromatic	3078	3074	3065	3071	3070	3070	3070	3074	3057
υ(C-H) alkan, alkene	2924,2855	2958,2924,2854	---	2956,2924,2853	2958,2924,2858	2958,2924,2854	2924,2854	2958,2924,2854	2967,2908,2806
υ(C-H) aldehyde	---	---	---	2772,2604,2559	2731, 2673, 2549	2673, 2549	2673, 2549	---	---
υ(C=O) aldehyde, carboxylic acid	---	---	1683	1687	1701	1697	1697	---	1744
υ(C=C) alkene, aromatic	1639	1643	1571	1603	1643	1643	1643	1639	1577
υ(C-C) in the ring	---	---	1508	---	---	---	---	---	1505
δ(C-H) scissoring	1462	1462	---	1453	1358	1458	1458	1462	---
δ (C-H) rocking	1381	1377	---	1377	1377	1377	1377	1377	---
υ(C-O)	---	---	1285	1326, 1291, 1179	1284, 1176, 1068	1319, 1284, 1176	1284, 1176, 1134	---	1296
δ(=C-H) bending	991, 910, 717	968, 887, 705	---	934, 809, 709	968, 891, 709	910,802,709	910, 802, 713	910, 887, 725	---

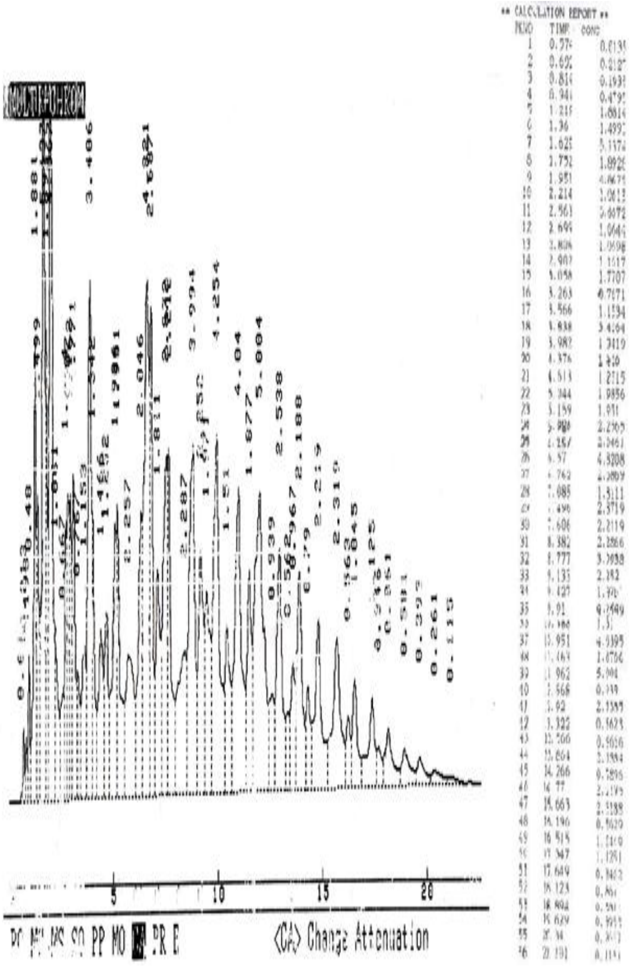
Gas chromatography *(GC) Analysis* :

Gas chromatography (GC ,PACKARD model :43817,UNITED) was used for the product analysis . Fig(13) from primary retention time and compare with retention time of ethanol in Fig (20) compounds began from carbon series C3-C14 and showed high concentrations down retention time 9 minutes and have some type of regularity, Fig (14) so began C3-

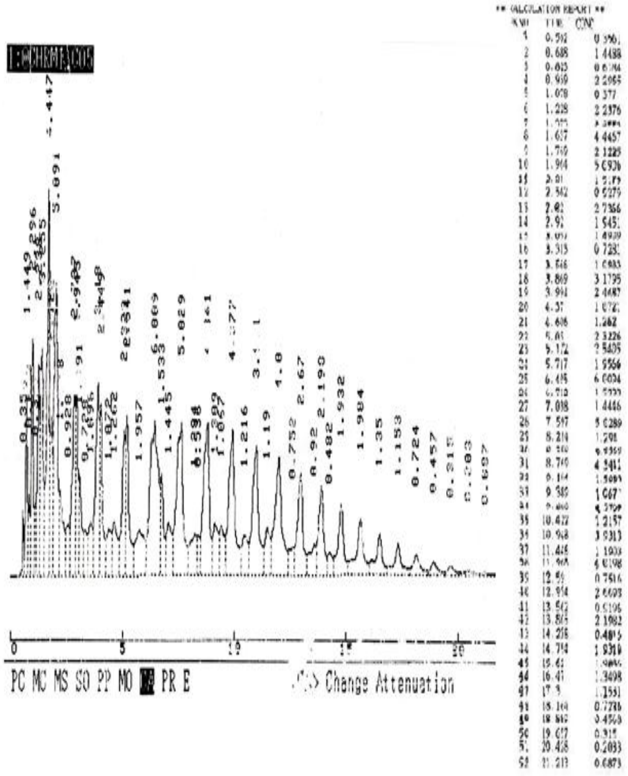
C14 and concentrations spread in irregularity form, Fig(15) it's too started from C3-C14 compounds concentration taking medium state between two previous states and lacking in compounds concentration up retention time 15 minutes, in Fig (16) compounds began from C3-C14 and seeming increasing in concentrations down retention time 5 minutes and decreasing in concentrations up retention time 5 minutes that emphases in Fig(19) appearing new compounds up retention time 5 minutes , Fig(17) so gave approximately same changes in Fig(16) , Fig(18) starting from C3-C14 and showed increasing in concentration down retention time 5 minutes and decreasing so clear in concentrations up retention time 5 minutes compare with Fig(15) so this back to new concentrations up retention time 5 minutes in Fig(19) . [9- 10].



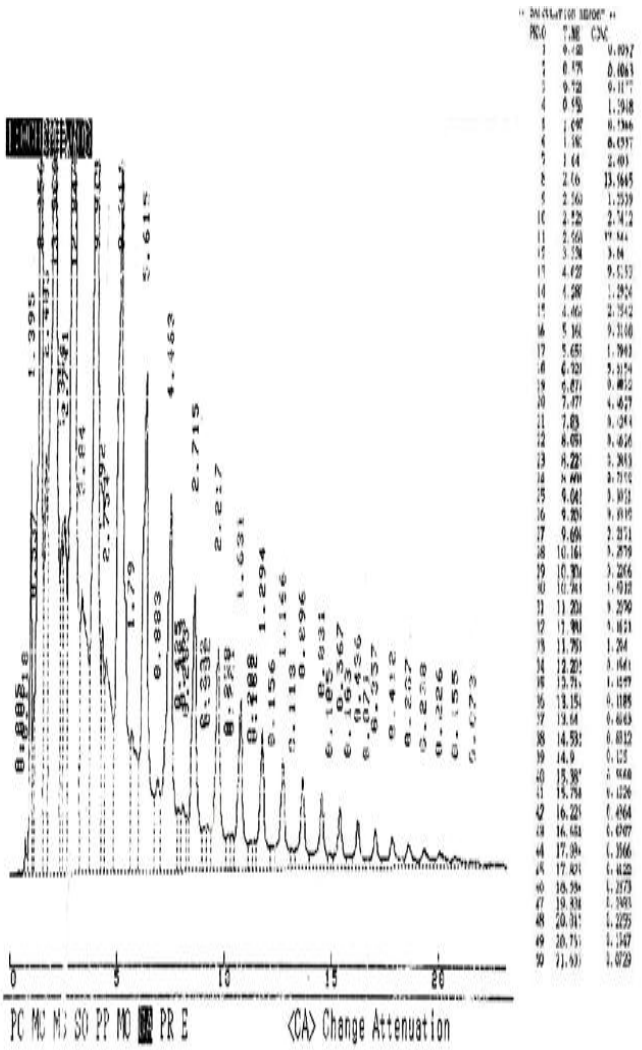
Figure(1٣):GC for liquid product of (PE).



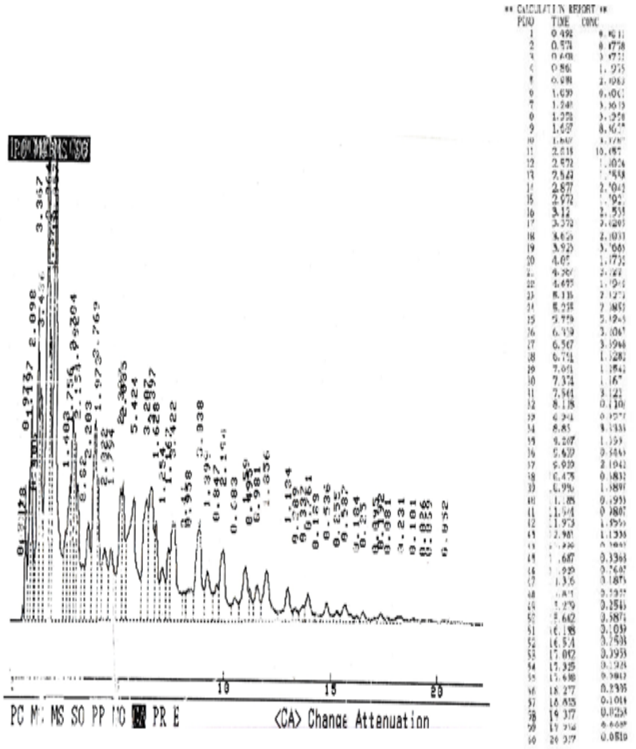
Figure(1٤):GC for liquid product of (PP).



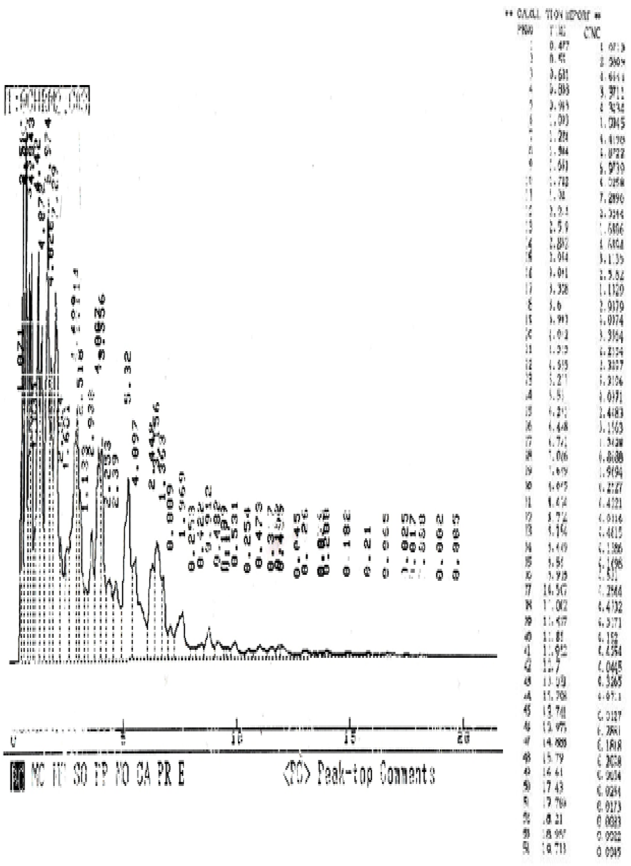
Figure(1٥):GC for liquid product of (PE+PP).



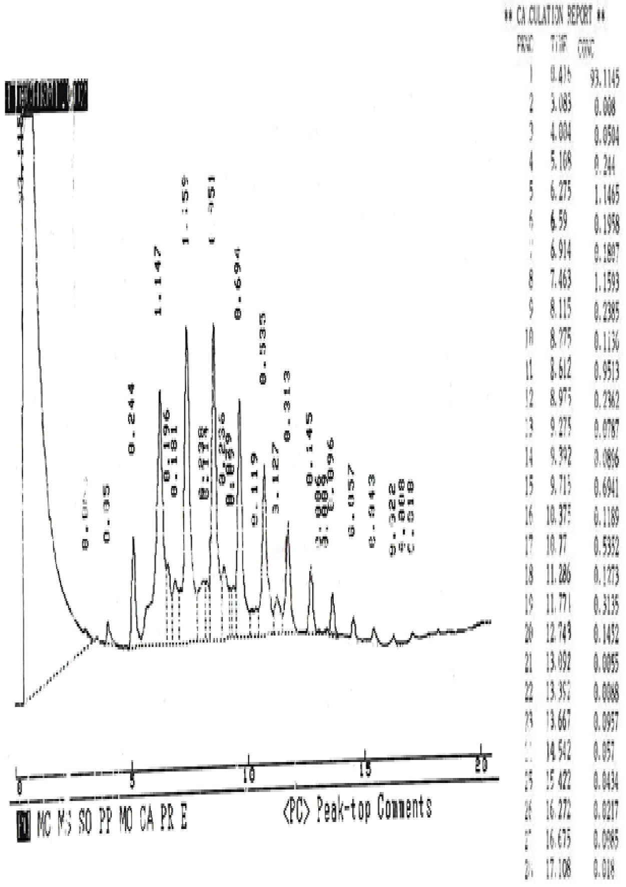
Figure(1٦):GC for liquid product of (PE+ PET).



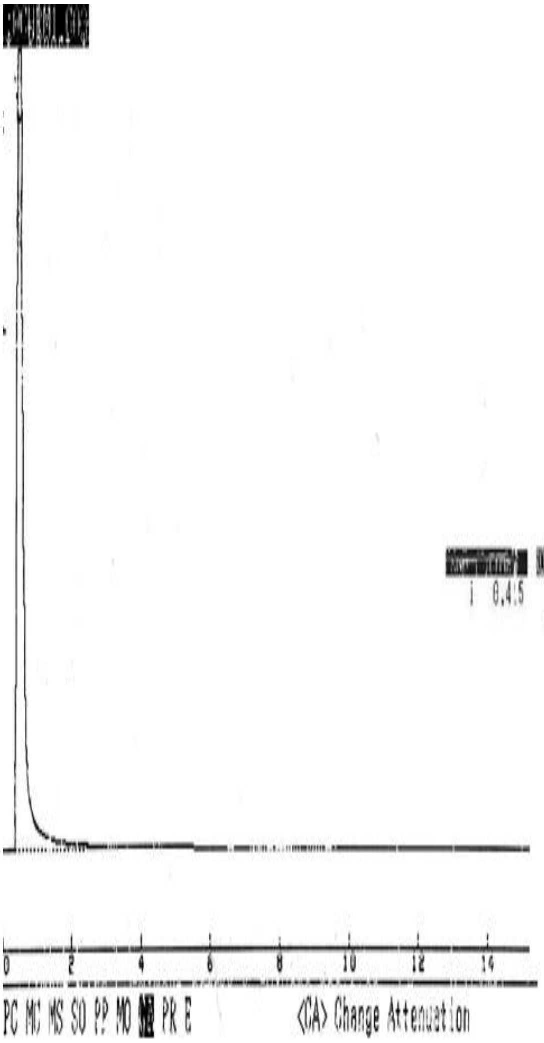
Figure(1٧):GC for liquid product of (PP+ PET).



Figure(1٨):GC for liquid product of (PE+PP+ PET).



Figure(1٩):GC for mixture of carbonyl compounds(Milky wax)dissolved in ethanol .



Figure(20):GC for ethanol .

Physical properties.

The data in Table (2) was constructed from Table (1) which shows AN increasing in conversion ratios of plastic wastes degradation. The results prove to be much better than individual product. Table (3) shows physical properties density(D=M/V) and boiling point for liquid products from degradation plastic wastes individually and combination of all. The results show a decreasing in density when degradation plastic wastes together, which made the product as a liquid fuel.

Table 1: Quantities of degradation products.

NO	Plastic wastes	Liquid (g)	Wax(g)	Coal(g)	Gases		Others (g)
					ml	g	
1	PE	14.37	20.1	2.06	470	0.3989	----
2	PP	9.91	11.93	5	180	0.1528	----
3	PET	-----	6.87	14.47	6597	5.5999	1.6*
4	PE+PP	27.35	55.68	5.61	624	0.5301	
5	PE+PET	4.39	19.31	12.5	4476	3.7999	3.67**
6	PP+ PET	4.12	23.29	24.6	4418	3.7499	4.69**
7	PE+PET+PP	18.5	30.02	46.44	6644	5.6400	19.5**

*** crystal powder atilt to yellow for terephthalic acid .**
**** mixture of carbonyl compounds(Milky wax) .**

Table 2 : Conversion and yields percentages of plastic waste products .

NO	Plastic wastes	Conversion (%)	Liquid yield(%)	Wax yield(%)	Coal yield(%)	Others yield (%)
1	PE	69.74	28.74	40.2	4.12	----
2	PP	43.99	19.82	23.86	10	----
3	PET	28.14	-----	13.74	28.94	3.2
4	PE+PP	83.56	27.35	55.68	5.61	----

5	**PE+PET**	**31.17**	**4.39**	**19.31**	**12.5**	**2.45**
6	**PP+ PET**	**35.85**	**4.12**	**23.29**	**24.6**	**3.13**
7	**PE+PET+PP**	**73.66**	**12..33**	**20.01**	**30.96**	**13**

Table 3: Specifications physical properties of degradation products.

Plastic wastes	Liquid	Wax	Coal	Others	Liquid Density(g/ml)	Liquid boiling Point (°C)
PE	**Clear yellow**	**Dark brown**	**Black powder**	**-------**	**0.767**	**48-108**
PP	**slight brown**	**Paly black**	**Paly black powder**	**-------**	**0.787**	**51-95**
PET	**-----**	**Semi solid brown**	**Porous shine solid**	**crystal powder atilt to yellow, Melting point >300°c**	**-----**	**-----**
PE+PP	**brown**	**Semi solid black**	**Black powder**	**------**	**0.755**	**53-89**
PE+PET	**Dark yellow**	**Slight brown**	**Mixture of powder and imporous solid**	**mixture of carbonyl compounds**	**0.784**	**40-67**
PP+ PET	**Dark brown**	**Semi solid olivary**	**Mixture of powder and imporous solid**	**mixture of carbonyl compounds**	**0.794**	**45-70**
PE+PET+PP	**Dark yellow change to Dark brown**	**Dark brown**	**Mixture of powder and imporous solid**	**mixture of carbonyl compounds**	**0.704** **0.686**	**48-70**

Table 4: Test results for the mixture of carbonyl compounds(Milky wax) .

(Brady`s test) For carbonyl group.	(Tollen`s test) For aldehyde.	($FeCl_3$ test) For carboxylic acid type .	(Baeyer`s test) for unsaturated bonds.	Solubility.	incineration
(+) yellow precipitate.	**(+)silver mirror**	**(+) brown atilt to red precipitate.**	**(+) brown precipitate**	**In organic solvents**	**White fume with black precipitate.**

Conclusions.

From results obtained from degradation of plastic wastes via vacuum pyrolysis (PP,PET, LDPE) individually and combination : degradation of PP, LDPE with privately form gave high concentrations of carbon compounds have long series either PET gave just solid materials, degradation together gave high concentrations of carbon compounds have short series and very low concentration of carbon compounds have long series also having same mixture product of same carbonyl compounds such carboxylic acid and unsaturated aldehyde that identified with primary form Table (4) .

References.

[1] G. Finnveden and others , "Life Cycle Assessments of Energy from Solid Waste", FOA Reprot, Ursvik ISSN; 1404-6520,2000.

[2] Mehmet Altan Kurnaz and Ayşegül Sağlam-Arslan, A Thematic Review of Some Studies Investigating Students'. Eurasian J. Phys. Chem. Educ. 3(1):51-74, 2011

[3] Vincenzo Giorgio Dovı, Ferenc Friedler Cleaner energy for sustainable future` Journal of Cleaner Production xxx, 1–7, 2009

[4] M. Sadikur Rahman, M. Verma" Agricultural waste plastics conversion into high energy liquid hydrocarbon fuel by thermal degradation process" Journal of Petroleum Technology and Alternative Fuels Vol. 2(8), pp. 141-145, August 2011.

[5] E.Ahmad, D. Kim. Catalytic degradation of waste plastic into fuel range hydrocarbons .International Journal of Chemical Research, ISSN: 0975-3699, Volume 1, Issue 2, pp-31- 36, 2009.

[6] M, Leenus Jesu Martin, V. Edwin Geo. Effect of diesel addition on the performance of oil fuelled DI diesel engine, Volume 2, Issue 2, pp.321-330, 2011

[7] Y.R.Sharma " elementary organin spectroscopy "4th edition by Rajendar Ravindar printers,2011.

[8]R. Morrison and R. Boyd ,"organic chemistry "3rd edition copyright by Allyn and Bacon.INC,1973.

[9] KU. Marek,A. Surma, JE. Walendziewski, Application of combustible wastes for the alternative fuels production. Polish Journal of Chemical Technology, 9, 4, 43 – 47, 2007

[10] Y. Zhou, L. Yongfeng, U. Zhang. Improved Hydrogen Storage Properties of LiBH4 Destabilized, J. Phys. Chem. C, 116, 1588–1595, 2012.

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تحطم الفضلات البلاستيكية (LDPE,PET, PP) لإنتاج الوقود السائل كطاقة بديلة باستخدام طريقة التحلل الحراري المفرغ .

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الخلاصة .

استخدم في هذا البحث الفضلات البلاستكية الأكثر تواجداً في البيئة وهي بولي بربيلين (PP) وبولي اثيلين تريفثاليت (PET) وبولي اثيلين واطئ الكثافة (LDPE). تم دراسة التحطم الحراري للمواد الثلاثة بشكل انفرادي والثلاثة مع بعض وتحت ظروف فراغية. شخص المنتج النهائي بواسطة جهاز كرموتوكرافيا الغاز (GC) وجهاز تحويلة فورير للاشعة تحت الحمراء (FTIR). تم قياس بعض الخواص الفيزيائية مثل الكثافة ودرجة الغليان. أظهرت النتائج أن المواد الثلاثة بصورة مجتمعة هو الأفضل في الحصول على الوقود السائل ذو الخصائص القريبة من المواصفات العالمية المطلوبة. وكذلك تم الحصول على ناتج مزيج من بعض المركبات الكاربونيلية كأحماض كاربوكسلية والدهايدات غير مشبعة والتي تم تشخيصها بصورة أولية.