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Research article

Liquid Fuels and Chemicals from Several Plastic Wastes and Motor Vehicle Tire Mixture by Catalytic Cracking

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Abstract

Waste plastics mixture and waste tire mixture to liquid fuel was recovery using ferric carbonate catalyst at temperature range 250 430 ºC. Raw materials were low density polyethylene, high density polyethylene, polypropylene, polystyrene and waste tire. In batch process experiment was conducted under laboratory fume hood with vacuum system. 50% waste plastics and 50% tire sample was use by weight and 2% ferric carbonate was added as a catalyst. Product fuel density is 0.78 gm/ml and fuel was analysis by GC/MS and hydrocarbon chain showed C_3-C_{20} including aromatic group. Experimental conversion rate showed liquid fuel conversion rate was 47.4%, light gas 14.9% and left over residue was 37.7%. Product fuel can use internal combustion engine or electricity production.

Keywords: tire, waste plastics, fuels, catalytic cracking, ferric carbonate, GC/MS

Introduction

Recycling and reusing of waste plastics has been of great interest in terms of the solution of their environmental and economic problems. Therefore, the utilization of a huge amount of waste plastic has been in the focus of investigations for the last 15 years. Plastic consumption was 150 Mt in 2000 worldwide, and it is estimated to be 258 Mt in 2010. Not only is the plastic consumption growing, but also the amount of wastes from them. In 2010, plastic consumption will be 75 Mt and the wastes 40 Mt only in Europe [1- 4]. In recent years, the quantity of solid wastes has increased significantly in both industrialized and developing countries, raising the question of the sustainability of disposal management [5]. This increase in waste accumulation is due to the substantial increase on energy demand and the consumption of natural resources and goods, caused by continuous growth of world population. These wastes need to be treated adequately to prevent environmental problems and make possible a sustained development of modern society [6, 7]. The decomposition of waste plastics into fuel represents a sustainable way for the recovery of the organic content of the polymeric waste and also preserves valuable petroleum resources in addition to protecting the environment [8].

The generation of used tires in 2005 was estimated to be 2.5 million tonnes in North America, 2.5 million in Europe, and 0.5-1.0 million in Japan, which means 6 kg (approximately the weight of a car tire) per inhabitant and year in these developed countries [9]. The forecast for 2012 is that world generation will exceed 17 million tonnes per year, given that economic growth in developing countries drives vehicle sales and the substitution of less deteriorated tires, and the measures adopted to lengthen tire life are insufficient to offset these circumstances [10]. China generated 1 million tonnes in 2005 and the annual increase is 12%. This outlook makes the valorization of used tires more interesting, and among the different technologies, pyrolysis has the following advantages: (i) it enables the subsequent individual valorization of gaseous, liquid, and carbon black fractions, which is an interesting aspect for economic viability; [11] (ii) it has a higher efficiency for energy and a lower environmental impact than incineration [12]. Different types of reactors have been used for tire pyrolysis, such as autoclaves [13] and fixed bed reactors,[14-18] and for a larger scale operation, bubbling fluidized bed reactors, [17-22] moving beds under vacuum, in one and two steps,[23-25] ablative beds, [26] and rotary ovens [27-29]. Key factors for process viability are high throughput and products with suitable properties for their subsequent valorization toward value added compounds such as high-quality carbon black, active carbon, or chemical compounds, such as benzene, toluene, xylene, limonene, and so on [30].

Materials and Experimental Process

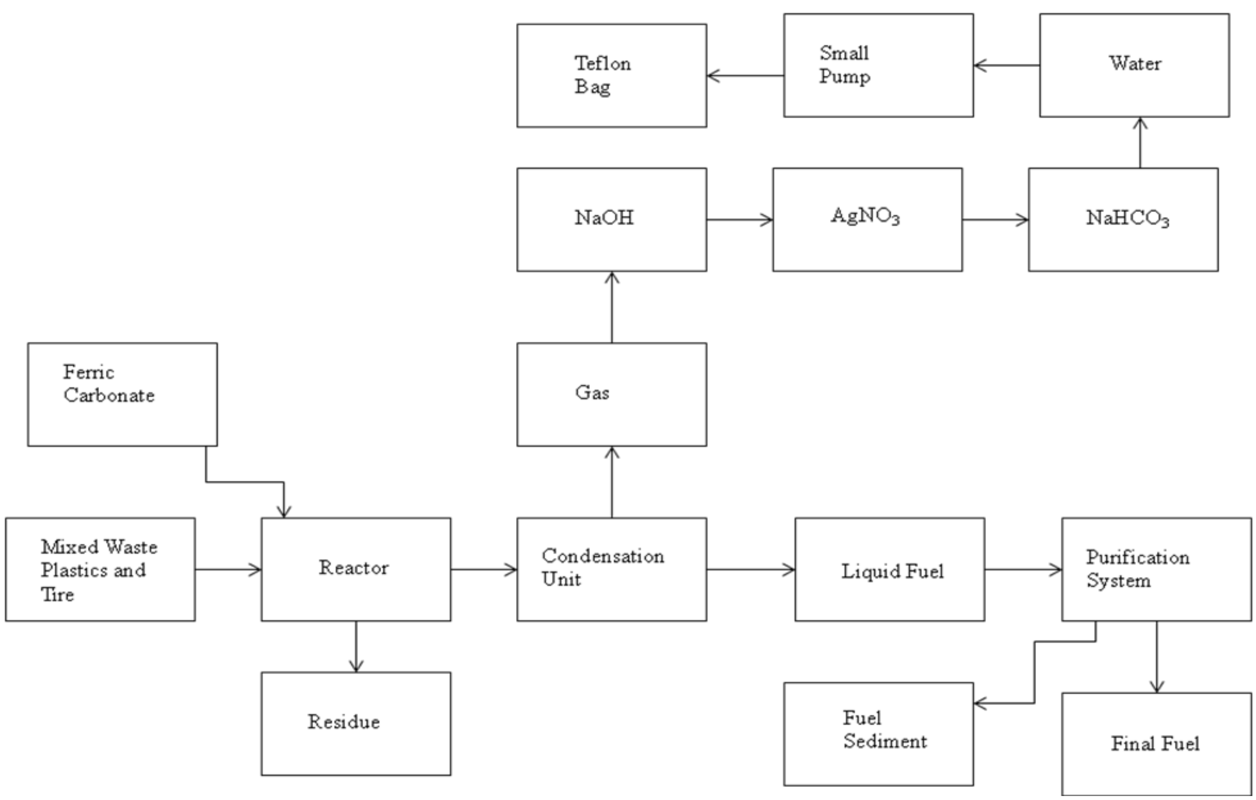

Figure 1: 50% mixed waste plastics and 50% tire mixture to fuel production process

Waste plastics and motor vehicle tire was collected from local city and collected waste plastics was LDPE, HDPE, PP and PS mixtures. Car used tire was collected from local collision center in Stamford. Collected waste materials shorted out manually and washout using laboratory sink. Waste plastics and tire was cut into small pieces for liquefaction process. Ferric carbonate prepared by laboratory and using sodium bicarbonate and ferric chloride and both chemical was collected from VWR.com Company. For experimental purpose sodium hydroxide, silver nitrate and sodium bicarbonate was provided from VWR.com Company.

Grounded waste materials were mixed with tire and LDPE, HDPE, PP, PS mixture. LDPE, HDPE, PP and PS mixture was use 50% and weight was 50 gm by weight, on the other hand used tire was use 50% and weight was 50 gm by weight. Waste plastics and tire mixture was total 100 gm by weight and ferric carbonate was 2gm and percentage was 2%. Experimental setup procedure shown into figure 1 and full setup was close system under laboratory fume hood. For experimental purpose ferric carbonate use as a catalyst and sodium hydroxide, silver nitrate and sodium bicarbonate was use for gas cleaning purpose. Sodium hydroxide, sodium bicarbonate and silver nitrate solution normality was 0.5 (N), 0.25 (N) and 0.25 (N). For waste plastic and motor vehicle waste materials to fuel production experimental setup purpose accessories and instrument was required such as glass reactor, temperature controller (variac meter), condensation unit, collection tank, fuel purification unit, final fuel collection tank, residue collection container, liquid solution container, small pump, Teflon bag. All accessories and part was connected and tighten enough to prevent gas lose during mixed waste plastics and tire mixture to fuel production. Experimental temperature range was 250 - 430 ºC and temperature controlled by variac meter. This experiment main goal was 50% waste plastics mixtures with 50% motor vehicle waste tire to fuel recovery percentage determine. Mixture waste plastics and tire to fuel product density is 0.78 g/ml and liquid fuel conversion rate was 47.4%, light gas 14.9% and left over residue was 37.7%. Residue percentage is showing high because tire has rubber, additives and fabric and rubber, additives and fabric percentage most likely 60% which is not convertible. Only petroleum portion was converted as a liquid fuel rest of percentage comes out as char or residue. In mass balance calculation result showed from 100 gm to liquid fuel weight 47.4 gm, gas converted 14.9 gm and solid black residue 37.7 gm. also high percentage additives present into polystyrene plastics which is 7- 9 %. Polystyrene plastic and tire additives and rest of plastics additives remain as solid black residue and all residues comes out after experiment finish. Sodium hydroxide, sodium bicarbonate and silver nitrate liquid solution was use for 14.9% light gas cleaning and finally light gas was passed through with clean water. Generated light gas was transferred into Teflon bag using pump and light gas can be use as heating source because light gas has hydrocarbon compounds such as methane, ethane, propane and butane. For experiment purpose input electricity was 0.711 KWh and time requirement was 4.50 hours. Ferric carbonate catalyst under recovery and light gas and residue analysis is under consideration.

Results and Discussions

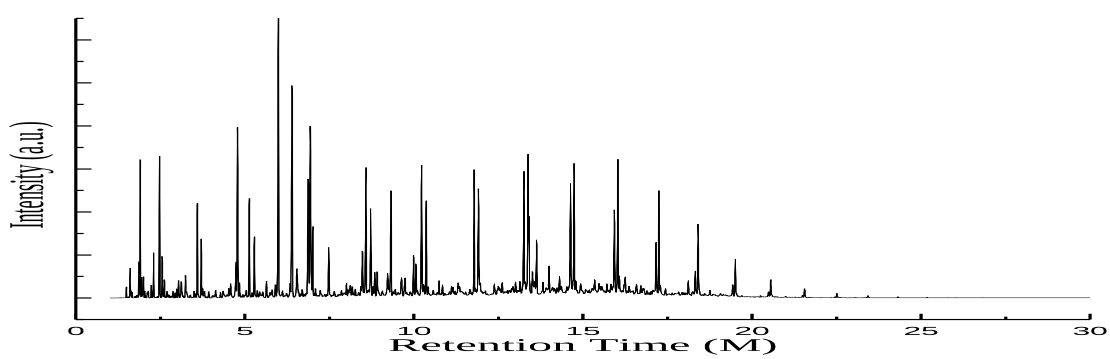

Figure 2: GC/MS chromatogram of mixed waste plastic and tire mixture into fuel

Table 1: GC/MS chromatogram compounds list of mixed waste plastic and tire mixture into fuel

Number of Peak	Retention Time (min.)	Trace Mass (m/z)	Compounds Name	Compound Formula	Molecular Weight	Probability %	NIST Library Number
1	1.49	41	Cyclopropane	C_3H_6	42	44.4	18854
2	1.56	43	Isobutane	C_4H_{10}	58	68.0	121
3	1.60	41	1-Propene, 2-methyl-	C_4H_8	56	26.1	61293
4	1.63	41	2-Butene, (E)-	C_4H_8	56	24.2	105
5	1.75	55	1-Butene, 3-methyl-	C_5H_{10}	70	17.4	160477
6	1.81	43	Butane, 2-methyl-	C_5H_{12}	72	69.5	61287
7	1.87	42	Cyclopropane, ethyl-	C_5H_{10}	70	22.8	114410
8	1.90	43	Pentane	C_5H_{12}	72	86.2	114462
9	1.94	55	2-Pentene	C_5H_{10}	70	20.3	19079
10	2.23	67	Bicyclo[2.1.0]pentane	C_5H_8	68	15.1	192491
11	2.30	43	Pentane, 2-methyl-	C_6H_{14}	86	63.3	61279
12	2.48	56	1-Hexene	C_6H_{12}	84	22.3	227613
13	2.55	57	Hexane	C_6H_{14}	86	85.9	61280
14	2.62	69	2-Pentene, 3-methyl-, (E)-	C_6H_{12}	84	17.0	19321
15	2.70	67	Cyclobutene, 3,3-dimethyl-	C_6H_{10}	82	9.16	62288
16	2.76	41	2-Pentene, 3-methyl-, (E)-	C_6H_{12}	84	20.9	19321
17	2.87	56	Cyclopentane, methyl-	C_6H_{12}	84	69.5	114428
18	2.94	67	1,3-Pentadiene, 2-methyl-, (E)-	C_6H_{10}	82	10.5	149695
19	2.98	79	1,3-Cyclopentadiene, 5-methyl-	C_6H_8	80	27.8	419
20	3.04	56	1-Pentene, 2,4-dimethyl-	C_7H_{14}	98	63.1	114435
21	3.12	67	Cyclopentene, 1-methyl-	C_6H_{10}	82	13.3	107747
22	3.24	78	Benzene	C_6H_6	78	70.7	114388
23	3.39	43	Hexane, 3-methyl-	C_7H_{16}	100	68.2	113081
24	3.50	67	Cyclohexene	C_6H_{10}	82	32.7	114431
25	3.59	56	1-Heptene	C_7H_{14}	98	39.2	107734
26	3.71	43	Heptane	C_7H_{16}	100	75.2	61276
27	3.75	81	1,3-Pentadiene, 2,4-dimethyl-	C_7H_{12}	96	12.2	114450
28	3.93	81	1,4-Hexadiene, 2-methyl-	C_7H_{12}	96	9.86	840
29	4.14	55	Cyclohexane, methyl-	C_7H_{14}	98	63.0	118503
30	4.24	69	Cyclopentane, ethyl-	C_7H_{14}	98	24.5	231044
31	4.36	79	2,4-Heptadien-1-ol, (E,E)-	$C_7H_{12}O$	112	7.91	1645
32	4.53	81	Cyclobutane, (1-methylethylidene)-	C_7H_{12}	96	13.8	150272
33	4.58	67	1-Heptene, 4-methyl-	C_8H_{16}	112	6.43	113433
34	4.74	43	Heptane, 4-methyl-	C_8H_{18}	114	62.3	113916
35	4.79	91	Toluene	C_7H_8	92	64.6	291301
36	4.84	81	Cyclohexene, 3-methyl-	C_7H_{12}	96	10.1	236066
37	5.13	55	1-Octene	C_8H_{16}	112	24.4	1604
38	5.28	43	Octane	C_8H_{18}	114	46.7	229407
39	5.37	55	2-Octene, (Z)-	C_8H_{16}	112	14.2	113889

40	5.64	43	Heptane, 2,4-dimethyl-	C_9H_{20}	128	33.8	155382
41	5.90	69	Cyclohexane, 1,3,5-trimethyl-, (1α,3α,5β)-	C_9H_{18}	126	18.5	2480
42	5.99	43	2,4-Dimethyl-1-heptene	C_9H_{18}	126	57.9	113516
43	6.40	91	Ethylbenzene	C_8H_{10}	106	57.6	158804
44	6.54	91	p-Xylene	C_8H_{10}	106	24.1	113952
45	6.87	43	1-Nonene	C_9H_{18}	126	18.1	107756
46	6.88	43	3-Octene, 2,2-dimethyl-	$C_{10}H_{20}$	140	6.29	186136
47	6.94	104	Styrene	C_8H_8	104	41.6	291542
48	7.01	43	Nonane	C_9H_{20}	128	39.6	228006
49	7.09	55	4-Nonene	C_9H_{18}	126	14.4	113904
50	7.48	105	Benzene, (1-methylethyl)-	C_9H_{12}	120	49.6	228742
51	7.64	55	2,4-Pentadien-1-ol, 3-propyl-, (2Z)-	$C_8H_{14}O$	126	10.6	142179
52	7.86	117	1,3-Methanopentalene, 1,2,3,5-tetrahydro-	C_9H_{10}	118	11.7	221371
53	8.01	91	Benzene, propyl-	C_9H_{12}	120	72.2	113930
54	8.12	105	Benzene, 1-ethyl-3-methyl-	C_9H_{12}	120	41.7	228743
55	8.48	118	α-Methylstyrene	C_9H_{10}	118	36.4	229186
56	8.58	56	1-Decene	$C_{10}H_{20}$	140	13.2	107686
57	8.73	57	Decane	$C_{10}H_{22}$	142	33.8	291484
58	8.80	55	2-Decene, (Z)-	$C_{10}H_{20}$	140	11.1	114151
59	8.85	71	Octane, 3,3-dimethyl-	$C_{10}H_{22}$	142	9.87	114124
60	9.23	119	2,3-Epoxycarane, (E)-	$C_{10}H_{16}O$	152	34.6	156146
61	9.32	68	D-Limonene	$C_{10}H_{16}$	136	31.2	62287
62	9.63	43	2-Undecanethiol, 2-methyl-	$C_{12}H_{26}S$	202	4.47	9094
63	9.73	91	Bicyclo[3.1.0]hex-3-en-2-ol, 2-methyl-5-(1-methylethyl)-, (1α,2α,5α)-	$C_{10}H_{16}O$	152	12.4	250249
64	9.99	69	Cyclooctane, 1,4-dimethyl-, trans-	$C_{10}H_{20}$	140	3.58	61408
65	10.23	55	Cyclopropane, 1-heptyl-2-methyl-	$C_{11}H_{22}$	154	5.65	62622
66	10.29	117	Benzene, 4-ethenyl-1,2-dimethyl-	$C_{10}H_{12}$	132	11.1	2980
67	10.36	57	Undecane	$C_{11}H_{24}$	156	33.0	114185
68	10.42	55	3-Undecene, (Z)-	$C_{11}H_{22}$	154	13.2	142598
69	10.58	55	2,4-Pentadien-1-ol, 3-pentyl-, (2Z)-	$C_{10}H_{18}O$	154	8.53	142197
70	10.85	69	Ethanone, 1-(1,2,2,3-tetramethylcyclopentyl)-, (1R-cis)-	$C_{11}H_{20}O$	168	4.54	186082
71	11.16	117	1b,5,5,6a-Tetramethyl-octahydro-1-oxa-cyclopropa[a]inden-6-one	$C_{13}H_{20}O_2$	208	8.90	194131
72	11.31	117	4-Methyl-α-methyl-α-nitrostyrene	$C_{10}H_{11}NO_2$	177	8.32	135064
73	11.78	55	1-Dodecene	$C_{12}H_{24}$	168	9.13	107688
74	11.91	57	Dodecane	$C_{12}H_{26}$	170	31.3	291499

75	12.38	57	Tetradecane, 2,6,10-trimethyl-	$C_{17}H_{36}$	240	10.0	11556
76	12.61	43	2-Hexyl-1-octanol	$C_{14}H_{30}O$	214	4.59	113807
77	13.13	55	7-Hexadecenal, (Z)-	$C_{16}H_{30}O$	238	12.5	293051
78	13.25	55	1-Tridecene	$C_{13}H_{26}$	182	9.92	107768
79	13.37	57	Tridecane	$C_{13}H_{28}$	184	19.9	107767
80	13.51	69	Trichloroacetic acid, hexadecyl ester	$C_{18}H_{33}Cl_3O_2$	386	3.21	280518
81	14.00	69	1-Decanol, 2-hexyl-	$C_{16}H_{34}O$	242	3.03	114709
82	14.64	55	1-Tetradecene	$C_{14}H_{28}$	196	6.08	69725
83	14.74	57	Tetradecane	$C_{14}H_{30}$	198	35.2	113925
84	15.34	71	Tetradecane, 2,6,10-trimethyl-	$C_{17}H_{36}$	240	14.9	11556
85	15.93	55	1-Pentadecene	$C_{15}H_{30}$	210	8.16	69726
86	16.03	57	Pentadecane	$C_{15}H_{32}$	212	33.5	107761
87	16.08	55	1-Dodecanol, 3,7,11-trimethyl-	$C_{15}H_{32}O$	228	4.50	22776
88	17.16	55	1-Hexadecene	$C_{16}H_{32}$	224	7.32	69727
89	17.25	57	Hexadecane	$C_{16}H_{34}$	226	38.7	114191
90	18.12	92	Benzene, 1,1'-(1,3-propanediyl) bis-	$C_{15}H_{16}$	196	91.5	133399
91	18.32	55	E-14-Hexadecenal	$C_{16}H_{30}O$	238	5.41	130980
92	18.41	57	Heptadecane	$C_{17}H_{36}$	240	26.2	107308
93	19.43	55	1-Eicosanol	$C_{20}H_{42}O$	298	4.85	113075
94	19.50	57	Octadecane	$C_{18}H_{38}$	254	18.8	57273
95	20.49	55	1-Nonadecene	$C_{19}H_{38}$	266	10.6	113626
96	20.55	57	Nonadecane	$C_{19}H_{40}$	268	28.7	114098
97	21.55	57	Eicosane	$C_{20}H_{42}$	282	13.6	290513

Waste plastics mixture and tire to liquid fuel was analysis by using only Gas chromatography and Mass Spectrometer (GC/MS) for compounds determination (Figure 2 and Table 1). GC/MS compounds were detected based one compound retention time (m) and trace mass (m/z). Product liquid fuel analysis result showed table 1 compound are present such as hydrocarbon group including alkane, alkene and alkyl group compounds, aromatic group, oxygen content, nitrogen content, alcoholic group or hydroxyl group and halogenated group compounds. GC/MS compound was traced by using NIST library and compounds probability percentage. In raw materials has additives and additives are using for plastics hardness, plastics softness, plastics color etc. In analysis result showed one compounds has chlorine and compounds name is Trichloroacetic acid, hexadecyl ester ($C_{18}H_{33}Cl_3O_2$) (t=13.51, m/z=69) and compounds molecular weight is 386 and probability percentage 3.11%. This compound comes out from additives because an additive has halogen stabilizers. In analysis compounds table showed one compound has sulfur content and compound name is 2-methyl-2-Undecanethiol ($C_{12}H_{26}S$) (t=9.63, m/z=43) compound molecular weight is 202 and compound probability percentage is 4.47%. All GC/MS traced compounds were detected carbon lower number to higher and molecular weight also low number to high. In this discussion section some compounds are elaborating based on retention time, compounds trace mass and probability percentage. Starting compound is Cyclopropane (C_3H_6) (t=1.49, m/z=41) compounds probability percentage is 44.4%, 2-methyl-1-Propene (C_4H_8) (t=1.60, m/z=41) compounds probability percentage is 26.1 %, 2-methyl-Butane (C_5H_{12}) (t=1.81, m/z=43) compounds probability percentage is 69.5%, 2-methyl-Pentane (C_6H_{14}) (t=2.30, m/z=43) compounds probability percentage is 63.3%, methyl-Cyclopentane (C_6H_{12}) (t=2.87, m/z=56) compounds probability percentage is 69.5 %, 2,4-dimethyl-1-Pentene (C_7H_{14}) (t=3.04, m/z=56) compounds probability percentage is 63.1 %, Benzene (C_6H_6) (t=3.24, m/z=78) compounds probability percentage is 70.7 %, Heptane (C_7H_{16}) (t=3.71, m/z=43) compounds probability percentage is 75.2 %, methyl-Cyclohexane (C_7H_{14}) (t=4.14, m/z=55) compounds probability percentage is 63.0 %, 4-methyl-Heptane (C_8H_{16}) (t=4.58, m/z=67) compounds probability percentage is 6.43 %, Toluene (C_7H_8) (t=4.79, m/z=91) compounds probability percentage is 64.6 %, Octane (C_8H_{18}) (t=5.28, m/z=43) compounds probability percentage is 46.7 %, 2,4-Dimethyl-1-heptene (C_9H_{18}) (t=5.99, m/z=43) compounds probability percentage is 57.9 %, Styrene (C_8H_8) (t=6.94, m/z=104) compounds probability percentage is 41.6 %, 1,2,3,5-tetrahydro-1,3-Methanopentalene (C_9H_{10}) (t=7.86, m/z=117) compounds probability percentage is 11.7 %, α-Methylstyrene (C_9H_{10}) (t=8.48, m/z=118) compounds probability percentage is 36.4 %, 3,3-dimethyl- Octane ($C_{10}H_{22}$) (t=8.58, m/z=71) compounds probability percentage is 9.87 %, D-Limonene ($C_{10}H_{16}$) (t=9.32, m/z=68) compounds probability percentage is 31.2%, 4-ethenyl-1,2-dimethyl-Benzene ($C_{10}H_{12}$) (t=10.29, m/z=117) compounds probability percentage is 11.1 %, (2Z)- 3-pentyl-2,4-Pentadien-1-ol ($C_{10}H_{18}O$) (t=10.58, m/z=55) compounds probability percentage is 8.53 %, 1-Dodecene ($C_{12}H_{24}$) (t=11.78, m/z=55) compounds probability percentage is 9.13 %, (Z)-7-Hexadecenal ($C_{16}H_{30}O$) (t=13.13, m/z=55) compounds probability percentage is 12.5 %, Tetradecane (14.74, m/z=57) compounds probability percentage is 35.2 %, Pentadecane ($C_{15}H_{32}$) (t=16.03, m/z=57) compounds probability percentage is 33.5 %, Hexadecane ($C_{16}H_{34}$) (t17.25, m/z=57) compounds probability percentage is 38.7 %, Heptadecane ($C_{17}H_{36}$) (t=18.41, m/z=57) compounds probability percentage is 26.2 %, 1-Nonadecene ($C_{19}H_{38}$) (t=20.49, m/z=55) compounds probability percentage is 10.6%, Eicosane ($C_{20}H_{42}$) (t=21.55, m/z=57) compounds probability percentage is 13.6 % respectively.

Conclusion

LDPE, HDPE, PP and PS waste plastics mixture with waste tire to fuel production was catalytic cracking and temperature was 250 - 430 ºC. Tire mixed with waste plastics production percentage is decrease because waste tire has high percentage of additives. Fuel color is light yellow and fuel was analysis by GC/MS and carbon chain was detected C_3 to C_{20}. Product fuel has aromatic group compounds and compounds are Benzene, Toluene, Ethylbenzene, p-Xylene, (1-methylethyl)-Benzene, propyl-Benzene, 1-ethyl-3-methyl-Benzene, α-Methylstyrene, 4-ethenyl-1,2-dimethyl-Benzene, bis-1, 1'-(1, 3-propanediyl) Benzene. Aromatic group percentage high because initial raw materials has polystyrene (PS) and tire both materials has aromatic group compounds. Fuel can use internal combustion engines and fuel can produce electricity using generator or power plant. Using present technology can convert waste plastic and tire to fuel and at a time can reduce waste plastics and waste tire problem from environment. Huge amount of waste plastics and waste tire are setting landfill or environment all of those waste plastic and waste tires can convert into valuable fuel sources. Its can create lot of job sector and boost up renewable/alternative energy sector and reduce some percentage of oil dependency.

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