COMPOSITION OF HYDROCARBON TYPE FUELS FORMED IN THERMAL DECOMPOSITION OF MUNICIPAL SOLID WASTE PLASTICS AND CALCIUM CARBONATE

Moinuddin Sarker[a]*, Mohammad Mamunor Rashid[a], Muhammad Sadikur Rahman[a]

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Random mixtures of waste plastics raw materials were thermolysed into liquid hydrocarbons at laboratory scales in a batch process by using a stainless steel reactor. Two series of experiments were carried out with random mixtures of waste plastics such as low and high density polyethylene, polypropylene, and polystyrene in the presence of 10 and 20 % calcium carbonate, respectively, at temperatures between 100 and 430 ºC. Four types of randomly mixed waste plastics were used in each series of experiments. The hydrocarbon oils formed were analyzed by using a gas chromatography and mass spectrometer (GC/MS) to determine the amounts and types of hydrocarbons. By using 10% calcium carbonate, the formed hydrocarbon mixture contained C_4 to C_{40} compounds while, in the presence of 20% calcium carbonate, the product consists of C_3 to C_{27} hydrocarbons determined by GC/MS analysis. Due to the high number of hydrocarbons in the oils formed in each series of thermal decomposition experiment, the oily products can be used as fuels for internal combustion engines or electric power plants.

* Corresponding Authors
Fax: (203) 406-9852
E-Mail: msarker@naturalstateresearch.com
[a] Natural State Research, Inc., Department of Research and Development, 37 Brown House Road (2nd Floor), Stamford, CT-06902, USA

Introduction

In 1993, waste plastics accounted for roughly 10% of all municipal solid waste (MSW) in the USA [1] with percentages in land filled MSW ranging from 15 to 25% depending upon location. The energy demand continuously increases and market structures evolve[2] as well, thus utilization of renewable energy sources such as wind and solar power has gained considerable importance since the oil crisis in the 1970s.[3] Europe's total energy consumption is expected to be covered by renewable energy sources in up to 10% by 2020[2], the remaining 90% still being dependent on fossil energy sources. Total waste production increased by about 10% in Europe between 1990 and 1995, with the annual amount estimated at 1.3 billion tons in 1995. The annual amount of hazardous waste was about 36 million tons.[4] In 2010, the amount of paper, glass, and plastic waste was expected to be about 60% higher than the 1990 levels, and the number of scrapped cars was expected to have grown 35% higher.[4] Landfill and incineration are common modes of waste treatment in most European countries[4] and co-incineration is commonly used particularly in the cement industry.[5,6]

The European waste directive called for a 30% reduction of waste amount land filled by 2010. Land filling of plastic wastes is undesirable due to poor biodegradability[7] of polymer materials and, on the other hand, these plastic wastes can be regarded as a potentially cheap source of chemicals and energy. The destruction of waste plastics by incineration, however, often generates problems with unacceptable emissions.

Chemical recycling proved to be a possible alternative strategy, when waste plastics are used as feedstock in various technologies, e.g. in converting them into basic petrochemicals used as chemical feedstock or fuels in a variety of downstream processes. There are two main chemical recycling routes, namely the thermal and the catalytic degradation.[8] Thermal cracking is a well-known technique and is often used in petrochemical processes. Thermal decomposition of waste plastics in the absence of oxygen can be carried out in various types of reactors such as shaft kilns, rotary kilns, screw conveyors, autoclaves, or fluidized beds.[9-12]

Including waste-to-energy (WTE) methods, only about 20% of all MSW was recovered in various recycling technologies, and only 15% of the plastics occurred in MSW were recovered in melting ("primary") and feedstock ("secondary" and "tertiary") type recycling methods. Secondary recycling can be defined as conversion to monomers or other building blocks, whereas, tertiary recycling means conversion to other chemical feedstock or fuels. Waste-to-energy methods (sometimes referred to as "quaternary recycling") are relatively cheap. Recently, another 20% of plastics occurred in MSW have been utilized in this way, however, it requires burning a large amount of non-renewable resources as well. Public perceptions regarding safety of incineration techniques prompted us and other researchers to collaborate under the auspices of the Consortium for Fossil Fuel Liquefaction Science (CFFLS), to investigate the feasibility of coal/waste plastics processing to liquid fuels or chemical feedstock. Obviously, dominant components of MSW-type waste plastics (mainly polyethylene, polystyrene, polyethylene terephthalate and polypropylene) are rich in carbon and hydrogen – basic building elements of petroleum – thus, searching possibilities to convert the waste plastics into liquid fuels seems to be a logical alternative of plastic recycling.[13,14]

Experiments

Materials

Random mixtures of waste plastic samples were collected in a local grocery store at Stamford City which consisted of low and high density polyethylene (HDPE and LDPE), polypropylene (PP) and polystyrene (PS). The samples were contaminated with foreign materials such as food particles, paper, dust, sand. Foreign components were separated out manually and the samples were washed with periodical adding of liquid soap into the washing water. Washing of plastics is not an essential step in our plastic-to-fuel process developed, but the laboratory scale process was performed with washed samples. Random mixtures of waste plastics containing both hard and soft plastic components were prepared by cutting the soft plastics and grinding the hard ones into pieces down to size 2-3 mm. Reagent grade anhydrous calcium carbonate powder was provided by AMRESCO Co.

Process Description

Grounded random mixtures of waste plastics were transferred into the reactor chamber together with calcium carbonate additive in amount of 10% or 20 % in each experiment, respectively. The weight of every mixture was controlled to be 1000 g. The reactor chamber and its cover were tightened with a screw system to prevent from gas leaking. A condensation unit and a fuel purification device were connected to the reactor and the fuel collection tanks, respectively. The upper outlet of the condensation unit was connected to a gas cleaning system. Light gases formed were transferred into a storage system and the sediment separated by the fuel purification device was recycled to the reactor as raw material. The heating temperature was controlled between 100 and 430 °C, respectively.

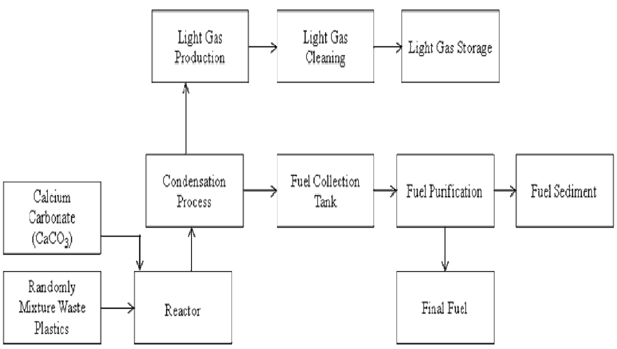

Figure 1: Random mixtures of waste plastics and calcium carbonate in the fuel production process

Calcium carbonate was used as additive in the reaction, but some acceleration effect was also observed. Waste plastics start to melt at 100 ºC and their melting was completed below 300 ºC. Long hydrocarbon chains broke down into short chain hydrocarbon due to heat treatment. The liquid slurry turned into vapour which condensed into a liquid hydrocarbon mixture. The reaction was not completed even at 300 °C, therefore, heating was continued until 430 ºC. The liquid hydrocarbon mixture formed was purified with an RCI fuel filter. Sediment was removed and reused in the next experiment as raw material. The light gas generated contained methane, ethane, propane, and butanes. The light gas formed was washed with sodium hydroxide solution. The density of the liquid formed with using 10 % calcium carbonate additive was determined as 0.78 g cm^{-3}. Yields of the products formed in the decomposition process carried out with 10 and 20 % calcium carbonate additive and 1 kg of plastics waste are shown in Table 1. When using 10% or 20 % calcium carbonate, 716.8 and 683.8 g liquid fuel, 155.1 and 98 g gas, and 128.1 and 218.2 g of solid residue were formed, respectively. It means that yields of liquid hydrocarbons, gases, and solid residues are 71,68 and 68.38 %, 15.51 and 9.8 %, 12.81 and 21.82 % in the experiments carried out with 10 and 20 % $CaCO_3$ content, respectively. The volumes of liquid phases were 922 ml and 870 ml starting form 1 kg of mixture, with 10 and 20 % of $CaCO_3$ content, respectively. Both experiments left back a black solid residue whose composition is under investigation.

Instrument

GC-MS analyses were performed on a Perkin-Elmer Clarus 500 instrument supplied with auto-sampler system. Elite-5 capillary column (30 meter length) and He as carrier gas were used. The injected volume was adjusted to be 5.0 µL, the sample split flow and the initial set point were 101.0 mL min^{-1} and 1.00 ml min^{-1}, respectively. The sample injector port temperature was adjusted to be 280 ºC, with 40 °C initial value. The temperature holding and equilibration times were 1 and 0.5 minutes, respectively. The temperature ramping was 10 ºC/ min up to 325 ºC and there was a holding for 15 minute at 325 ºC. The mass spectrometer was operated in EI+ mode, between 35.00 and 528.00 m/z units with 0.25 s scan and 0.15 s interscan times.

Results and Discussion

GC-MS analyses of liquids formed in the reaction of randomly mixed waste plastics and 10% calcium carbonate (Fig. 2 and Table 2) showed the occurrence of a variety of components. Many compounds detected contained carbon atoms within the range between C_3 and C_{27}. Based on the retention times and fragmentation patterns, different types of compounds such as hydrocarbons, halogen compounds, oxygenated compounds, and nitrogen containing compounds were identified. The GC-MS analyses showed presence of such characteristic compounds as 3-butene-1-ol (C_4H_8O) (t=1.50, m/z=41), cis-1,2-dimethylcyclopropane (C_5H_{10}) (t=2.02, m/z=55), cis-1-ethyl-2-methylcyclopropane (C_6H_{12}) (t=2.50, m/z=41), Z,Z-2,4-hexadiene (C_6H_{10}) (t= 2.96, m/z= 67), 4-methyl-1,4-hexadiene (C_7H_{12}) (t=3.77, m/z=81), 2-methyl-1,4-hexadiene (C_7H_{12}) (t=3.95, m/z=81), norbornane (C_7H_{12}) (t=4.44, m/z=81), 3-methylcyclohexene (C_7H_{12}) (t=4.86, m/z=81), 1α,3α,5α-

1,3,5-trimethylcyclohexane (C_9H_{18}) (t= 5.92, m/z= 69), styrene (C_8H_8) (t=6.95, m/z=104), 3-decyn-2-ol ($C_{10}H_{18}O$) (t=7.92, m/z=57), 4-methyldecane ($C_{11}H_{24}$) (t=8.85, m/z=43), cis-1,4-dimethylcyclooctane ($C_{10}H_{20}$)

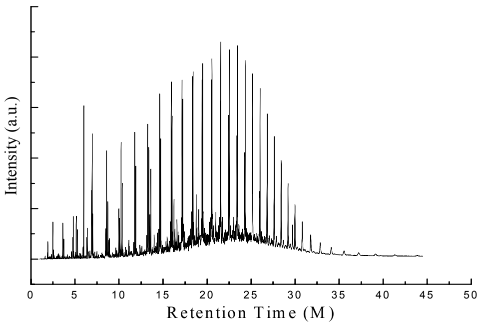

Figure 2: GC/MS chromatogram of the liquid product formed in the presence of 10 % CaCO3 containing random waste plastics in the mixture

(t=9.99, m/z=41), 1R-cis-1-(1,2,2,3-tetramethylcyclopentyl)-ethanone ($C_{11}H_{20}O$) (t=10.74, m/z=43), dodecane ($C_{12}H_{26}$) (t=11.91, m/z=57), N-[4-bromo-n-butyl]-2-piperidinone ($C_9H_{16}BrN$) (t=12.50, m/z=41), 4,6,8-trimethyl-1-nonene ($C_{12}H_{24}$) (t=13.63, m/z=43), 7-tetradecene ($C_{14}H_{28}$) (t=14.78, m/z=41), 1-hexadecene ($C_{16}H_{32}$) (t=15.93, m/z=41). Different kinds of hydrocarbons were formed containing aliphatic and aromatic rings, single and double bonds such as octadecane ($C_{18}H_{38}$) (t=20.56, m/z=85), octadecene ($C_{18}H_{38}$) (t=23.44, m/z=85), isomeric octadecanes ($C_{18}H_{38}$) (t=24.33, 25.19, 26.83, 28.41, m/z=57), heptacosanes ($C_{27}H_{56}$) (t=30.82, 32.87, m/z=57, and t=35.56, m/z=44), benzene (C_6H_6), toluene (C_7H_8), styrene (C_8H_8), 1-methylethylbenzene (C_9H_{12}), 1-ethyl-3-methylbenzene (C_9H_{12}), α-methylstyrene (C_9H_{10}), 1-ethenyl-2-methylbenzene (C_9H_{10}) etc..

Some alcoholic groups containing products such as 1-eicosanol ($C_{20}H_{42}O$) (t= 21.75, m/z=55) could also be detected. Dyes and additives occurring in the raw waste plastics had no influence on quality of the produced fuel-like liquid products.

The experiments were carried out without evacuation of the reactor space, thus the humidity as oxygen source might be responsible for the formation of some oxygen–containing products.

Table 1: Product yields in thermal decomposition of waste plastics in the presence of calcium carbonate

Sample weight (g.)	$CaCO_3$ % (m/m)	Fuel weight (g)	Fuel volume (ml)	Residue weight (g.)	Sample as light gas weight (g.)	Fuel Yield % (m/m)	Light gas Yield % (m/m)	Residue Yield % (m/m)
1000	10	716.8	922	128.1	155.1	71.68	15.51	12.81
1000	20	683.8	870	218.2	98	68.38	9.8	21.82

Table 2: GC/MS chromatogram compound list of liquid product formed in thermal decomposition of random waste plastics and 10% calcium carbonate mixture

No. of Peak	Retention Time (min.)	Trace Mass (m/z)	Compound Name	Compound Formula	Molecular Weight	Probability %	NIST Library Number
1	1.50	41	3-Buten-1-ol	C_4H_8O	72	17.7	114446
2	1.60	41	2-Butene	C_4H_8	56	23.4	61292
3	1.64	41	1-Propene, 2-methyl-	C_4H_8	56	19.3	61293
4	1.87	42	Cyclopropane, ethyl-	C_5H_{10}	70	23.2	19072
5	1.91	43	Pentane	C_5H_{12}	72	88.0	114462
6	1.96	55	2-Pentene	C_5H_{10}	70	15.0	19079
7	2.02	55	cis-1,2-dimethyl Cyclopropane	C_5H_{10}	70	25.0	19070
8	2.06	67	1,3-Pentadiene	C_5H_8	68	17.1	61941
9	2.13	67	1,4-Pentadiene	C_5H_8	68	13.1	209
10	2.25	67	Cyclopentene	C_5H_8	68	19.7	19032
11	2.32	43	Pentane, 2-methyl-	C_6H_{14}	86	42.7	61279
12	2.50	41	cis-1-ethyl-2-methyl Cyclopropane	C_6H_{12}	84	18.9	113658
13	2.58	57	Hexane	C_6H_{14}	86	67.2	61280
14	2.64	69	2-Pentene, 3-methyl-, (Z)-	C_6H_{12}	84	13.8	114483
15	2.68	41	3-Hexen-1-ol, (Z)-	$C_6H_{12}O$	100	6.68	114154
16	2.72	67	4-Penten-1-ol, 3-methyl-	$C_6H_{12}O$	100	15.5	113673
17	2.84	67	2,4-Hexadiene, (Z,Z)-	C_6H_{10}	82	7.79	113646

18	2.90	56	Cyclopentane, methyl-	C_6H_{12}	84	59.9	114428
19	2.96	67	2,4-Hexadiene, (Z,Z)-	C_6H_{10}	82	13.1	113646
20	3.06	56	1-Pentene, 2,4-dimethyl-	C_7H_{14}	98	49.4	114435
21	3.14	67	Cyclopentene, 3-methyl-	C_6H_{10}	82	25.1	114408
22	3.27	78	Benzene	C_6H_6	78	66.3	114388
23	3.38	79	1,3-Cyclohexadiene	C_6H_8	80	23.0	118700
24	3.52	67	Cyclohexene	C_6H_{10}	82	31.6	114431
25	3.57	56	1-Hexene, 2-methyl-	C_7H_{14}	98	35.9	114433
26	3.62	41	cis-1,2-dimethyl-Cyclopentane	C_7H_{14}	98	26.8	114027
27	3.73	43	Heptane	C_7H_{16}	100	47.6	61276
28	3.77	81	1,4-Hexadiene, 4-methyl-	C_7H_{12}	96	14.4	113135
29	3.95	81	1,4-Hexadiene, 2-methyl-	C_7H_{12}	96	7.17	840
30	4.07	81	Cyclobutane, (1-methylethylidene)-	C_7H_{12}	96	6.41	150272
31	4.16	83	Cyclohexane, methyl-	C_7H_{14}	98	54.1	118503
32	4.30	69	Cyclopentane, ethyl-	C_7H_{14}	98	28.7	940
33	4.38	79	1-Cyclohexene-1-methanol	$C_7H_{12}O$	112	16.9	52048
34	4.44	81	Norbornane	C_7H_{12}	96	7.51	114371
35	4.51	56	2,4-Dimethyl-1-hexene	C_8H_{16}	112	31.6	113443
36	4.55	81	Cyclobutane, (1-methylethylidene)-	C_7H_{12}	96	13.8	150272
37	4.60	67	3-Heptene, 4-methyl-	C_8H_{16}	112	7.60	114150
38	4.75	43	Heptane, 4-methyl-	C_8H_{18}	114	62.3	113916
39	4.80	91	Toluene	C_7H_8	92	41.5	291301
40	4.86	81	Cyclohexene, 3-methyl-	C_7H_{12}	96	9.86	236066
41	5.06	56	1-Heptene, 2-methyl-	C_8H_{16}	112	45.1	113675
42	5.15	41	1-Octene	C_8H_{16}	112	16.9	1604
43	5.23	95	Cyclopropane, (2,2-dimethylpropylidene)-	C_8H_{14}	110	8.35	60981
44	5.29	43	Octane	C_8H_{18}	114	36.7	229407
45	5.39	55	3-Octene, (Z)-	C_8H_{16}	112	11.5	113895
46	5.46	41	4-Methyl-1,4-heptadiene	C_8H_{14}	110	7.53	113473
47	5.55	69	cis-1,1,3,4-tetramethyl-Cyclopentane	C_9H_{18}	126	14.6	34789
48	5.65	43	Hexane, 3-ethyl-	C_8H_{18}	114	15.8	113940
49	5.80	67	1-Methyl-2-methylenecyclohexane	C_8H_{14}	110	26.7	113437
50	5.92	69	Cyclohexane, 1,3,5-trimethyl-, (1α,3α,5α)-	C_9H_{18}	126	24.4	114126
51	6.01	70	2,4-Dimethyl-1-heptene	C_9H_{18}	126	49.5	113516
52	6.35	69	Cyclohexane, 1,3,5-trimethyl-, (1α,3α,5β)-	C_9H_{18}	126	37.2	2480
53	6.40	91	Ethylbenzene	C_8H_{10}	106	66.0	114918
54	6.55	91	Cyclohexanol, 1-ethynyl-, carbamate	$C_9H_{13}NO_2$	167	35.5	313023
55	6.71	67	cis-1,4-Dimethyl-2-methylenecyclohexane	C_9H_{16}	124	12.2	113533
56	6.88	41	1-Nonene	C_9H_{18}	126	10.5	107756
57	6.95	104	Styrene	C_8H_8	104	33.8	291542
58	7.02	43	Nonane	C_9H_{20}	128	31.3	228006
59	7.10	55	4-Nonene	C_9H_{18}	126	8.07	113904
60	7.24	55	3-Octyne, 2-methyl-	C_9H_{16}	124	4.17	62452
61	7.44	67	Ethylidenecycloheptane	C_9H_{16}	124	5.69	113500
62	7.49	105	Benzene, (1-methylethyl)-	C_9H_{12}	120	22.7	228742
63	7.52	67	1-Cyclohexyl-1-pentyne	$C_{11}H_{18}$	150	5.42	114866
64	7.66	55	Cyclopentane, butyl-	C_9H_{18}	126	9.72	114172
65	7.86	67	Cyclopentene, 1-butyl-	C_9H_{16}	124	9.34	113491
66	7.92	57	3-Decyn-2-ol	$C_{10}H_{18}O$	154	8.40	53449

67	8.01	91	Benzene, propyl-	C_9H_{12}	120	56.2	113930
68	8.07	57	Octane, 2,3-dimethyl-	$C_{10}H_{22}$	142	17.3	114135
69	8.13	105	Benzene, 1-ethyl-3-methyl-	C_9H_{12}	120	10.7	228743
70	8.43	41	E-1,6-Undecadiene	$C_{11}H_{20}$	152	11.7	245712
71	8.49	118	α-Methylstyrene	C_9H_{10}	118	31.4	30236
72	8.59	41	1-Decene	$C_{10}H_{20}$	140	16.6	118883
73	8.73	57	Decane	$C_{10}H_{22}$	142	49.6	114147
74	8.85	43	Decane, 4-methyl-	$C_{11}H_{24}$	156	15.8	113875
75	8.92	43	Octane, 3,3-dimethyl-	$C_{10}H_{22}$	142	11.1	61706
76	9.27	117	Benzene, 1-ethenyl-2-methyl-	C_9H_{10}	118	10.6	118193
77	9.64	41	2-Undecanethiol, 2-methyl-	$C_{12}H_{26}S$	202	4.45	9094
78	9.74	91	2-Cyclohexen-1-ol, 2-methyl-5-(1-methylethenyl)-	$C_{10}H_{16}O$	152	16.3	114684
79	9.99	41	cis-1,4-dimethyl-Cyclooctane	$C_{10}H_{20}$	140	3.73	61409
80	10.06	41	Diisoamylene	$C_{10}H_{20}$	140	4.19	3659
81	10.24	41	2-Undecene, (Z)-	$C_{11}H_{22}$	154	6.19	142596
82	10.37	43	Undecane	$C_{11}H_{24}$	156	42.5	114185
83	10.43	55	5-Undecene, (E)-	$C_{11}H_{22}$	154	10.0	114227
84	10.74	43	1R-cis- 1-(1,2,2,3-tetramethylcyclopentyl)-Ethanone	$C_{11}H_{20}O$	168	5.54	186082
85	11.06	91	9-Hexadecenoic acid, phenylmethyl ester, (Z)-	$C_{23}H_{36}O_2$	344	6.61	67839
86	11.12	69	1,12-Tridecadiene	$C_{13}H_{24}$	180	6.65	7380
87	11.16	41	Z-10-Pentadecen-1-ol	$C_{15}H_{30}O$	226	5.48	245485
88	11.67	41	6-Dodecene, (Z)-	$C_{12}H_{24}$	168	5.06	142611
89	11.78	41	3-Dodecene, (E)-	$C_{12}H_{24}$	168	9.21	113960
90	11.91	57	Dodecane	$C_{12}H_{26}$	170	25.2	291499
91	12.38	43	Dodecane, 2,6,10-trimethyl-	$C_{15}H_{32}$	212	6.60	68892
92	12.50	41	2-Piperidinone, N-[4-bromo-n-butyl]-	$C_9H_{16}BrNO$	233	5.17	251632
93	13.14	41	Z-10-Pentadecen-1-ol	$C_{15}H_{30}O$	226	15.4	245485
94	13.25	41	2-Tridecene, (E)-	$C_{13}H_{26}$	182	8.35	142614
95	13.37	43	Hexadecane	$C_{16}H_{34}$	226	9.77	114191
96	13.40	41	3-Tridecene, (Z)-	$C_{13}H_{26}$	182	2.47	142615
97	13.51	43	Trifluoroacetic acid, n-heptadecyl ester	$C_{17}H_{31}F_3O_2$	324	2.78	216792
98	13.63	43	1-Nonene, 4,6,8-trimethyl-	$C_{12}H_{24}$	168	2.61	6413
99	13.99	43	1-Tetracosanol	$C_{24}H_{50}O$	354	2.76	16001
100	14.36	55	1,12-Tridecadiene	$C_{13}H_{24}$	180	7.61	7380
101	14.52	41	Z-10-Pentadecen-1-ol	$C_{15}H_{30}O$	226	22.9	245485
102	14.63	41	1-Tetradecene	$C_{14}H_{28}$	196	5.12	34720
103	14.74	43	Tetradecane	$C_{14}H_{30}$	198	19.5	113925
104	14.78	41	7-Tetradecene	$C_{14}H_{28}$	196	4.34	70643
105	15.47	43	2-Piperidinone, N-[4-bromo-n-butyl]-	$C_9H_{16}BrNO$	233	4.48	251632
106	15.70	43	7-Hexadecenal, (Z)-	$C_{16}H_{30}O$	238	6.85	293051
107	15.83	41	Z-10-Pentadecen-1-ol	$C_{15}H_{30}O$	226	22.7	245485
108	15.93	41	1-Hexadecene	$C_{16}H_{32}$	224	5.58	118882
109	16.02	43	Hexadecane	$C_{16}H_{34}$	226	22.0	114191
110	16.07	41	10-Heneicosene (c,t)	$C_{21}H_{42}$	294	3.04	113073
111	16.25	43	Trichloroacetic acid, hexadecyl ester	$C_{18}H_{33}Cl_3O_2$	386	3.59	280518
112	16.71	43	2-Piperidinone, N-[4-bromo-n-butyl]-	$C_9H_{16}BrNO$	233	3.16	251632
113	17.07	41	Z-10-Pentadecen-1-ol	$C_{15}H_{30}O$	226	14.0	245485

114	17.16	55	1-Hexadecene	$C_{16}H_{32}$	224	6.90	118882
115	17.25	43	Hexadecane	$C_{16}H_{34}$	226	18.3	114191
116	17.29	41	10-Heneicosene (c,t)	$C_{21}H_{42}$	294	3.40	113073
117	17.44	41	E-2-Octadecadecen-1-ol	$C_{18}H_{36}O$	268	4.70	131102
118	18.24	41	Z-10-Pentadecen-1-ol	$C_{15}H_{30}O$	226	14.8	245485
119	18.33	55	1-Nonadecene	$C_{19}H_{38}$	266	5.66	113626
120	18.41	71	Nonadecane	$C_{19}H_{40}$	268	12.6	114098
121	19.44	41	1-Nonadecene	$C_{19}H_{38}$	266	6.60	113626
122	19.51	43	Heneicosane	$C_{21}H_{44}$	296	9.78	107569
123	20.43	55	1-Docosanol	$C_{22}H_{46}O$	326	5.85	23377
124	20.56	85	Octadecane	$C_{18}H_{38}$	254	9.09	57273
125	21.50	55	1-Docosene	$C_{22}H_{44}$	308	9.78	113878
126	21.56	43	Octadecane	$C_{18}H_{38}$	254	7.19	57273
127	21.70	43	Hexadecane, 1,1-bis(dodecyloxy)-	$C_{40}H_{82}O_2$	594	6.93	36104
128	21.75	55	1-Eicosanol	$C_{20}H_{42}O$	298	3.91	113075
129	22.46	43	1-Docosene	$C_{22}H_{44}$	308	17.5	113878
130	23.39	55	1-Docosene	$C_{22}H_{44}$	308	18.6	113878
131	23.44	85	Octadecane	$C_{18}H_{38}$	254	8.86	57273
132	24.28	55	1-Docosene	$C_{22}H_{44}$	308	12.0	113878
133	24.33	57	Octadecane	$C_{18}H_{38}$	254	7.39	57273
134	25.14	55	1-Docosene	$C_{22}H_{44}$	308	9.40	113878
135	25.19	57	Octadecane	$C_{18}H_{38}$	254	4.95	57273
136	26.01	57	Hexacosane	$C_{26}H_{54}$	366	4.48	107147
137	26.83	57	Octadecane	$C_{18}H_{38}$	254	5.08	57273
138	27.62	57	Heptacosane	$C_{27}H_{56}$	380	5.54	150574
139	28.41	57	Octadecane	$C_{18}H_{38}$	254	4.59	57273
140	29.19	57	Heptacosane	$C_{27}H_{56}$	380	4.94	150574
141	29.72	306	1,1':3',1''-Terphenyl, 5'-phenyl-	$C_{24}H_{18}$	306	50.4	57402
142	29.98	57	Heneicosane, 11-(1-ethylpropyl)-	$C_{26}H_{54}$	366	4.62	16318
143	30.82	57	Heptacosane	$C_{27}H_{56}$	380	7.17	79427
144	31.77	57	Heptacosane	$C_{27}H_{56}$	380	7.88	79427
145	32.87	57	Heptacosane	$C_{27}H_{56}$	380	9.78	79427
146	34.12	57	Heptacosane	$C_{27}H_{56}$	380	10.9	79427
147	35.56	44	Heptacosane	$C_{27}H_{56}$	380	8.06	79427

Table 3: GC/MS chromatogram compound list of liquid product formed in thermal decomposition of random waste plastics and 20% calcium carbonate mixture

No. of Peak	Retention Time (M)	Trace Mass (m/z)	Compounds Name	Compounds Formula	Molecular Weight	Probability %	NIST Library Number
1	1.49	41	Cyclopropane	C_3H_6	42	50.1	18854
2	1.60	41	1-Propene, 2-methyl-	C_4H_8	56	23.3	61293
3	1.61	43	Butane	C_4H_{10}	58	18.2	61290
4	1.63	41	2-Butene	C_4H_8	56	20.5	61292
5	1.83	67	1,4-Pentadiene	C_5H_8	68	21.5	114494
6	1.87	42	2-Pentene, (E)-	C_5H_{10}	70	21.1	291780
7	1.91	43	Pentane	C_5H_{12}	72	85.8	114462
8	1.95	55	cis-1,2-dimethyl-Cyclopropane	C_5H_{10}	70	23.8	19070
9	2.07	67	1,4-Pentadiene	C_5H_8	68	19.4	114494
10	2.26	67	Cyclopentene	C_5H_8	68	15.8	19032
11	2.32	43	Butane, 2,3-dimethyl-	C_6H_{14}	86	13.9	291518
12	2.50	41	1-Hexene	C_6H_{12}	84	15.3	500
13	2.58	57	Hexane	C_6H_{14}	86	68.7	61280
14	2.64	41	2-Pentene, 3-methyl-, (Z)-	C_6H_{12}	84	12.5	114483
15	2.72	67	1,3-Butadiene, 2-ethyl-	C_6H_{10}	82	18.8	118159
16	2.84	67	2,4-Hexadiene, (Z,Z)-	C_6H_{10}	82	9.94	113646

17	2.90	56	Cyclopentane, methyl-	C_6H_{12}	84	69.2	114428
18	2.96	67	1,3-Pentadiene, 2-methyl-, (E)-	C_6H_{10}	82	12.1	113652
19	3.01	79	3-Vinyl-1-cyclobutene	C_6H_8	80	13.3	214892
20	3.06	79	1,3-Cyclopentadiene, 5-methyl-	C_6H_8	80	13.9	419
21	3.15	67	Cyclopentene, 3-methyl-	C_6H_{10}	82	18.8	114408
22	3.20	41	1-Hexene, 5-methyl-	C_7H_{14}	98	9.13	918
23	3.27	78	Benzene	C_6H_6	78	69.0	114388
24	3.32	67	Cyclobutene, 3,3-dimethyl-	C_6H_{10}	82	7.04	62288
25	3.38	79	1,4-Cyclohexadiene	C_6H_8	80	16.5	114497
26	3.42	43	Hexane, 3-methyl-	C_7H_{16}	100	62.7	113081
27	3.45	81	Dihydromyrcene	$C_{10}H_{18}$	138	5.24	292831
28	3.52	67	Cyclohexene	C_6H_{10}	82	27.0	114431
29	3.58	56	1-Hexene, 2-methyl-	C_7H_{14}	98	34.5	114433
30	3.62	41	1-Heptene	C_7H_{14}	98	28.1	107734
31	3.74	43	Heptane	C_7H_{16}	100	46.5	61276
32	3.78	81	Cyclopropane, trimethylmethylene-	C_7H_{12}	96	9.46	63085
33	3.84	55	2-Heptene	C_7H_{14}	98	33.7	113119
34	3.89	41	2-Hexene, 3-methyl-, (Z)-	C_7H_{14}	98	7.85	114046
35	3.96	81	2,3-Dimethyl-1,4-pentadiene	C_7H_{12}	96	8.68	113670
36	4.07	81	Cyclopentane, 1-methyl-2-methylene-	C_7H_{12}	96	12.6	62523
37	4.17	83	Cyclohexane, methyl-	C_7H_{14}	98	60.0	118503
38	4.31	69	Cyclopentane, ethyl-	C_7H_{14}	98	49.6	940
39	4.39	79	1-Cyclohexene-1-methanol	$C_7H_{12}O$	112	18.5	52048
40	4.44	81	Norbornane	C_7H_{12}	96	6.07	114371
41	4.50	79	1,3,5-Heptatriene, (E,E)-	C_7H_{10}	94	15.3	118126
42	4.55	81	Cyclopentene, 4,4-dimethyl-	C_7H_{12}	96	14.4	38642
43	4.61	67	Cyclopentane, ethylidene-	C_7H_{12}	96	22.5	151340
44	4.76	43	Heptane, 4-methyl-	C_8H_{18}	114	59.6	113916
45	4.81	91	Toluene	C_7H_8	92	37.6	291301
46	4.87	81	Cyclohexene, 3-methyl-	C_7H_{12}	96	10.6	236066
47	4.96	67	Cyclopropane, (2-methylenebutyl)-	C_8H_{14}	110	6.19	62733
48	5.01	41	1,4-Octadiene	C_8H_{14}	110	26.5	113431
49	5.07	56	1-Heptene, 2-methyl-	C_8H_{16}	112	27.3	113675
50	5.15	41	1-Octene	C_8H_{16}	112	27.6	1604
51	5.23	55	2-Octyn-1-ol	$C_8H_{14}O$	126	12.2	113247
52	5.30	43	Octane	C_8H_{18}	114	35.6	229407
53	5.39	55	3-Octene, (Z)-	C_8H_{16}	112	12.3	113895
54	5.55	83	cis-1,1,3,4-tetramethyl-Cyclopentane	C_9H_{18}	126	12.4	34789
55	5.92	69	Cyclohexane, 1,3,5-trimethyl-, (1α,3α,5β)-	C_9H_{18}	126	20.1	2480
56	6.00	43	2,4-Dimethyl-1-heptene	C_9H_{18}	126	55.7	113516
57	6.35	69	Cyclohexane, 1,3,5-trimethyl-, (1α,3α,5β)-	C_9H_{18}	126	31.6	2480
58	6.40	91	Ethylbenzene	C_8H_{10}	106	70.8	114918
59	6.55	91	Cyclohexanol, 1-ethynyl-, carbamate	$C_9H_{13}NO_2$	167	29.4	313023
60	6.70	41	Cyclohexane, 1-propenyl-	C_9H_{16}	124	11.0	26935
61	6.78	70	Heptane, 3-methylene-	C_8H_{16}	112	6.46	60836
62	6.88	41	cis-2-Nonene	C_9H_{18}	126	11.0	113508
63	6.94	104	Styrene	C_8H_8	104	37.5	291542

64	7.02	43	Nonane	C_9H_{20}	128	29.7	228006
65	7.10	55	4-Nonene	C_9H_{18}	126	11.6	113904
66	7.24	55	2-Octyn-1-ol	$C_8H_{14}O$	126	10.5	113247
67	7.66	55	Cyclopentane, butyl-	C_9H_{18}	126	16.1	114172
68	7.87	67	Cyclopentene, 1-butyl-	C_9H_{16}	124	41.1	113491
69	8.43	41	1,9-Decadiene	$C_{10}H_{18}$	138	14.3	118291
70	8.49	118	Azetidine, 3-methyl-3-phenyl-	$C_{10}H_{13}N$	147	32.0	4393
71	8.59	41	1-Decene	$C_{10}H_{20}$	140	13.7	118883
72	8.73	57	Decane	$C_{10}H_{22}$	142	52.8	114147
73	8.81	55	2-Decene, (Z)-	$C_{10}H_{20}$	140	11.6	114151
74	8.85	43	Decane, 4-methyl-	$C_{11}H_{24}$	156	10.8	5261
75	8.92	43	Octane, 3,5-dimethyl-	$C_{10}H_{22}$	142	9.96	114062
76	9.39	41	2,4-Pentadien-1-ol, 3-pentyl-, (2Z)-	$C_{10}H_{18}O$	154	6.46	142197
77	9.75	91	Bicyclo[3.1.1]heptan-3-ol, 6,6-dimethyl-2-methylene-, [1S-(1α,3α,5α)]-	$C_{10}H_{16}O$	152	15.3	151861
78	9.99	41	1-Octene, 3,7-dimethyl-	$C_{10}H_{20}$	140	3.22	3653
79	10.06	41	5-Tridecene, (Z)-	$C_{13}H_{26}$	182	5.28	142618
80	10.24	41	1-Undecene	$C_{11}H_{22}$	154	7.34	5022
81	10.30	41	E-10-Pentadecenol	$C_{15}H_{30}O$	226	4.48	245484
82	10.37	43	Undecane	$C_{11}H_{24}$	156	48.2	114185
83	10.43	41	3-Undecene, (Z)-	$C_{11}H_{22}$	154	9.86	142598
84	10.58	41	2-Decyn-1-ol	$C_{10}H_{18}O$	154	9.00	53366
85	11.06	41	4-Chloro-3-n-hexyltetrahydropyran	$C_{11}H_{21}ClO$	204	13.2	216835
86	11.12	69	2-Isopropenyl-5-methylhex-4-enal	$C_{10}H_{16}O$	152	6.71	191046
87	11.16	41	1b,5,5,6a-Tetramethyl-octahydro-1-oxa-cyclopropa[a]inden-6-one	$C_{13}H_{20}O_2$	208	6.62	194131
88	11.66	41	Z-1,8-Dodecadiene	$C_{12}H_{22}$	166	7.63	245715
89	11.79	41	3-Dodecene, (E)-	$C_{12}H_{24}$	168	9.43	113960
90	11.91	43	Dodecane	$C_{12}H_{26}$	170	22.1	291499
91	12.38	41	2-Piperidinone, N-[4-bromo-n-butyl]-	$C_9H_{16}BrNO$	233	3.98	251632
92	12.49	41	Z-10-Pentadecen-1-ol	$C_{15}H_{30}O$	226	6.62	245485
93	12.62	41	1-Nonadecanol	$C_{19}H_{40}O$	284	4.45	13666
94	13.14	41	Z-10-Pentadecen-1-ol	$C_{15}H_{30}O$	226	8.47	245485
95	13.26	41	2-Tridecene, (E)-	$C_{13}H_{26}$	182	7.28	142614
96	13.37	43	Tetradecane	$C_{14}H_{30}$	198	13.6	113925
97	13.51	43	4-Trifluoroacetoxytridecane	$C_{15}H_{27}F_3O_2$	296	2.38	245473
98	13.63	43	1-Octanol, 2-butyl-	$C_{12}H_{26}O$	186	3.49	114639
99	14.36	41	1,12-Tridecadiene	$C_{13}H_{24}$	180	6.25	7380
100	14.53	41	Z-10-Pentadecen-1-ol	$C_{15}H_{30}O$	226	11.8	245485
101	14.64	41	7-Tetradecene, (E)-	$C_{14}H_{28}$	196	4.90	142631
102	14.74	43	Tetradecane	$C_{14}H_{30}$	198	18.4	113925
103	14.79	41	7-Tetradecene	$C_{14}H_{28}$	196	5.46	70643
104	15.48	41	1-Nonadecanol	$C_{19}H_{40}O$	284	8.74	13666
105	15.94	55	1-Hexadecene	$C_{16}H_{32}$	224	6.29	118882
106	16.03	43	Hexadecane	$C_{16}H_{34}$	226	21.5	114191
107	16.08	41	E-2-Hexadecacen-1-ol	$C_{16}H_{32}O$	240	4.99	131101
108	17.17	41	1-Hexadecene	$C_{16}H_{32}$	224	5.93	118882
109	17.26	41	Hexadecane	$C_{16}H_{34}$	226	17.8	114191
110	17.29	41	1-Hexadecene	$C_{16}H_{32}$	224	4.10	118882
111	17.45	41	10-Heneicosene (c,t)	$C_{21}H_{42}$	294	3.10	113073
112	18.25	41	Z-10-Pentadecen-1-ol	$C_{15}H_{30}O$	226	13.1	245485
113	18.34	83	1-Nonadecene	$C_{19}H_{38}$	266	5.65	113626

114	18.42	43	Octadecane	$C_{18}H_{38}$	254	11.2	57273
115	18.45	55	10-Heneicosene (c,t)	$C_{21}H_{42}$	294	5.31	113073
116	18.76	43	Trichloroacetic acid, hexadecyl ester	$C_{18}H_{33}Cl_3O_2$	386	5.30	280518
117	19.07	43	1-Docosanol	$C_{22}H_{46}O$	326	5.25	23377
118	19.44	55	1-Nonadecene	$C_{19}H_{38}$	266	6.65	113626
119	19.52	43	Nonadecane	$C_{19}H_{40}$	268	12.2	114098
120	19.70	43	1-Decanol, 2-hexyl-	$C_{16}H_{34}O$	242	9.73	114709
121	20.43	55	E-2-Octadecadecen-1-ol	$C_{18}H_{36}O$	268	13.1	131102
122	20.50	55	1-Nonadecene	$C_{19}H_{38}$	266	10.1	113626
123	20.57	85	Heptadecane	$C_{17}H_{36}$	240	9.96	107308
124	21.50	55	1-Docosene	$C_{22}H_{44}$	308	9.51	113878
125	21.57	57	Nonadecane	$C_{19}H_{40}$	268	10.3	114098
126	22.47	83	1-Docosene	$C_{22}H_{44}$	308	11.8	113878
127	22.52	57	Nonadecane	$C_{19}H_{40}$	268	7.43	114098
128	23.39	55	1-Docosene	$C_{22}H_{44}$	308	18.1	113878
129	23.44	43	Nonadecane	$C_{19}H_{40}$	268	5.88	114098
130	24.29	55	1-Docosene	$C_{22}H_{44}$	308	14.8	113878
131	24.33	43	Eicosane	$C_{20}H_{42}$	282	6.10	290513
132	25.14	43	1-Docosene	$C_{22}H_{44}$	308	12.0	113878
133	25.19	57	Octadecane	$C_{18}H_{38}$	254	5.34	57273
134	26.02	57	Hexacosane	$C_{26}H_{54}$	366	5.27	107147
135	26.83	57	Nonadecane	$C_{19}H_{40}$	268	4.38	114098
136	27.62	57	Eicosane, 2-methyl-	$C_{21}H_{44}$	296	5.46	113884
137	28.40	57	Octadecane	$C_{18}H_{38}$	254	5.41	57273
138	29.17	57	Heneicosane, 11-(1-ethylpropyl)-	$C_{26}H_{54}$	366	4.02	16318
139	29.95	57	Heptacosane	$C_{27}H_{56}$	380	4.35	79427
140	30.78	57	1-Decanol, 2-hexyl-	$C_{16}H_{34}O$	242	3.96	113815
141	31.72	57	1-Heptacosanol	$C_{27}H_{56}O$	396	4.82	16909
142	32.79	57	Heptacosane	$C_{27}H_{56}$	380	6.95	79427
143	34.02	57	1-Heptacosanol	$C_{27}H_{56}O$	396	8.96	16909
144	35.45	57	10-Octadecenal	$C_{18}H_{34}O$	266	4.84	36160
145	37.09	57	1-Heptacosanol	$C_{27}H_{56}O$	396	9.81	16909

GC-MS results of the liquid product formed in thermal decomposition of the mixture containing 20 % $CaCO_3$ and waste plastics can be seen in Fig. 3 and Table 3.

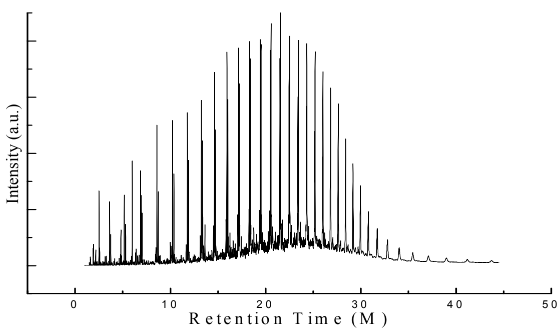

Figure 3: GC/MS chromatogram of liquid product formed in thermal decomposition of the mixture containing 10 % $CaCO_3$ and random waste plastics

The analysis showed the presence of a variety of compounds formed with carbon atoms between C_3 and C_{27}. Based on the retention times and fragmentation patterns, hydrocarbons, as well as halogen, oxygen, or nitrogen containing organic compounds were detected. The most important hydrocarbon constituents found were cyclopropane (C_3H_6) (t=1.49, m/z=41), 2-butene (C_4H_8) (t= 1.63, m/z=41), cis-1,2-dimethylcyclopropane (C_5H_{10}) (t=1.95, m/z=55), hexane (C_6H_{14}) (t=2.58, m/z= 57), methylcyclopentane (C_6H_{12}) (t=2.90, m/z=56), 2-methyl-1-hexene (C_7H_{14}) (t=3.58, m/z=56), methylcyclohexane (C_7H_{14}) (t=4.17, m/z=83), 1-octene (C_8H_{16}) (t=5.15, m/z=41), 1α,3α,5β-1,3,5-trimethyl-cyclohexane(C_9H_{18}) (t=5.92, m/z=69), decane ($C_{10}H_{22}$) (t=8.73, m/z=57), undecane ($C_{11}H_{24}$) (t=0.37, m/z=43), dodecane ($C_{12}H_{26}$) (t= 11.91, m/z=43), tetradecane ($C_{14}H_{30}$) (t=14.74, m/z=43), nonadecanes ($C_{19}H_{40}$) (t=19.52 and t=21.57, m/z=43), eicosane ($C_{20}H_{42}$) (t=24.33, m/z=43), 11-(1-ethylpropyl)-heneicosane ($C_{26}H_{54}$) (t=29.17, m/z=57). Different kinds of aromatic compounds such as benzene (C_6H_6) (t= 3.27, m/z=78), toluene (C_7H_8) (t=4.81, m/z=91), and styrene (C_8H_8) (t=6.94, m/z=104) were mainly found in the liquid products formed from wastes containing polystyrene. Oxygen-containing compounds such as cyclohexenenylmethanol ($C_7H_{12}O$) (t=4.39, m/z=79), Z-10-pentadecen-1-ol ($C_{15}H_{30}O$) (t=18.25, m/z=41), or 1-heptacosanol ($C_{27}H_{56}O$) (t=34.02, m/z=57) could also be detected. Some halogen containing products such as N-[4-bromo-n-butyl]-2-piperidinone ($C_9H_{16}BrNO$) (t=12.38, m/z=41) were probably formed due to presence of additives or dyes in the waste plastics.

Conclusion

Thermal degradation of random mixtures of waste plastics containing low and high density polyethylene, polypropylene, and polystyrene, and 10% or 20% calcium carbonate in a steel reactor at temperatures 100-430 °C resulted in a fuel-like liquid decomposition product. GC/MS studies showed that, in the presence of 10% or 20 % calcium carbonate, the fuel-like hydrocarbon ranges were found to be C_4-C_{40} or C_3-C_{27}, respectively. Both liquid fractions contain mainly aromatic and aliphatic hydrocarbons such as benzene (C_6H_6), toluene(C_7H_8), ethylbenzene (C_8H_{10}), propylbenzene (C_9H_{12}), α-methylstyrene (C_9H_{10}), and 1-ethenyl-2-methylbenzene (C_9H_{10}). When using a higher amount (20 %) of $CaCO_3$, the amount of residue increased and the amount of light gas and liquid products decreased, with the liquid seeming to be thicker.

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References

[1] Characterization of Municipal Solid Waste in the United States, **1994**, Update, EPA Report 530-R-94-042.

[2] Bailey, R. (ed.), European Energy to 2020, European Communities, Luxembourg, **1996**, Report No. 92/827/ 5226/7. Part 3.

[3] Pereia, M. Energias renovaveis (Renewable energies), Sociedade Portuguesa de Energia Solar, Lisbon, **1998**.

[4] European Topic Center on Waste, Waste Generation and Management, European Environment Agency, Copenhagen, **1999,** Chapter 3.

[5] European Union's Framework Program-ENERGIE, The Use of Industrial Waste as Alternative Fuels in the Cement Industry, Institute for the Diversification and Saving of Energy, Madrid, **2000**, Report No. DIS- 1289-97-ES.

[6] Kikuchi, r., Sato, H., Matsukura, Y., Yamamoto, T. Fuel Process. Technol., **2005**, *86*, 1279.

[7] Scott, G. Polymers and the environment. London: Royal Society of Chemistry, **1999**.

[8] Brandrup, J., Bittner, M., Michaeli, W., Menges, G. Recycling and recovery of plastics. Munich, New York: Carl Hanser Verlag, **1996**.

[9] Kaminsky, W., Schlesselmann, B., Simon, C. J Anal Appl Pyrolysis **1995**, *32*, 19.

[10] Sodero S. F, Berruti F., Behie L. A. Chem. Eng. Sci. **1996**, *51*, 2805.

[11] Mastellone, M. L., Perugini, F., Ponte, M., Arena, U.. Polym. Degrad. Stab., **2002**, *76*(3), 479.

[12] Yeuh-Hui Lin, Polym. Degrad. Stab., **2009**, *94*, 1924.

[13] Huffman, G. P., Feng, Z., Mahajan, V., Sivakumar, P., Jung, H., Tiemey J. W. and Wender I. Am. Chem. Sot., Div. Fuel Chem., Prepr., **1995**, *40*(l), 34.

[14] Liu, K., Meuzelaar, H. L. C. Fuel Process. Technol. **1996**, *49*, 1.

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