Chemical Products Produced from High Density Polyethylene (HDPE) Waste Plastic

Moinuddin Sarker¹, Mohammad Mamunor Rashid², Muhammad Sadikur Rahman³, Mohammed Molla⁴
Natural State Research, Inc. Department of Research and Development, 37 Brown House Road (2nd Floor), Stamford, CT 06902, USA

¹msarker@naturalstateresearch.com; ²mamun@naturalstateresearch.com; ³sadik@naturalstateresearch.com; ⁴mmolla@naturalstateresearch.com

Abstract-Waste high density polyethylene (HDPE) in the form of liquid detergent bottles (white color) was used for this experiment to obtain naphtha grade fuel. The final product consisted of 30% naphtha product in volume and the rest was other grade fuel. The temperature range for the entire liquefaction process was 100-450°C. The naphtha chemical product was collected between 110-135°C. A glass reactor was used for experiment and the fractional column was also glass system and fractional glass was Pyrex glass. Produced chemical product was analyzed by gas chromatography and mass spectrometer and FT-IR. They were used to identify the chemical products band energy determination. Produced naphtha product has short and long chain aliphatic hydrocarbon and chemical product, density is 0.74 gm/ml and it has good Btu value and sulfur content meets the standards according to EPA. This chemical product could be used as a feed stock for other chemical production purposes.

Keywords- Chemical Product; Waste Plastic; High Density Polyethylene; HDPE; Thermal Degradation

I. INTRODUCTION

Currently US generates a large quantity of waste plastics and waste tires each year. All these wastes are discarded and end up in sanitary landfills. As per older standards, only 4% of the waste plastics are reused. Waste plastics occupy approximately 21 vol.% of US landfills as per 1995 survey [1]. Increasing the recycling rate of plastic will require innovative and cost-effective recycling technologies. Recycling plastic back to fundamental feedstock has been one area of active research and shows promise in overcoming many problems plaguing the conventional recycling process. These new technologies have been called "feedstock recycling" or "advanced recycling technologies" and include process such as methanolysis of polyesters and thermal depolymerization of polyolefins [4-6]. Advanced technologies, specifically the depolymerization of polyolefins seems to be the most effective in converting the large amount of waste plastic to resourceful source.

Waste plastic recycling can be categorized into four modes. Primary recycling deals with conversion into products similar in nature to the original product. Secondary recycling involves conversion into products of different forms for less demanding applications. Tertiary recycling converts wastes into basic chemicals or feedstock. Quaternary recycling retrieves energy from wastes through combustion. An example of the last type is incineration of wastes for power generation. Secondary recycling, which

involves grinding, remelting and re-forming of the waste materials into lower-value products such as fillers and fibers, has been a more common practice for waste plastic until now ^[6-11]. Even though these methods are currently being applied, the feasibility of these methods in the future is not very possible. The slim possible chance is due to the large amount of waste plastic that is generated, and also different plastics have different types of characteristics which make it difficult to apply the different recycling methods ^[12-14].

Thermal degradation of converting waste plastic to liquid hydrocarbon materials is an economically and environmentally accepted method for converting the large amount of waste plastics. The products of such processes are liquid mixtures of hydrocarbons boiling in the temperature range 35-360 °C, gaseous hydrocarbons as well as solid residue, similar to wax and coke. Through the years excellent results have been obtained from liquefaction of individual polymers (Polyethylene (PE), Polypropylene (PP), Polystyrene (PS) etc.) and relatively clean mixed plastics using solid acid catalysts and metal-promoted solid acid catalysts. For example, Venkatesh et al. [3] and Shabtai et al.[4] have obtained high yields of liquids that consist predominantly of isoalkanes in the gasoline boiling range from HDPE, PP, and PS at relatively low temperature (300-375°C) using similar metal catalysts mentioned above. In this particular study, we are conducting a thermal degradation process utilizing waste high density polyethylene as a raw material. High density polyethylene is a large part of the waste plastic composition. One particular difference in this study was that no forms of catalysts were utilized during the conversion process. The conversion process is described in detail in the method section.

II. MATERIALS & METHOD

A. Materials

Waste plastic collected from local municipalities were mixed with HDPE, LDPE code and non-coded such as grocery bag, milk container, juice container, liquid detergent bottle etc. Waste plastics were a mixture of soft shape and hard shape. Collected waste plastic included foreign materials. Separated all kind of foreign materials and washed with soap then cut into small pieces manually. HDPE waste plastic was use for this experiment as a raw materials and it was wash with water and liquid detergent. HDPE waste plastic was detergent bottle and it was hard shape plastic and HDPE plastic color was white color.

B. Experimental Process

HDPE white color liquid detergent bottle was used for liquefaction process by using small glass reactor with fractional distillation column. Liquefaction temperature range for liquefaction process was 100~450 °C. HDPE waste plastics were cut into small pieces and put into the reactor to set up the fractional distillation column with various temperatures to collect different grade fuels. Fig.1 showed chemical product collection process. Glass fractional distillation column set up with reactor and chemical naphtha was collected. Number 11 in the diagram is where the naphtha chemical is collected. Reactor temperature was monitored using variac. Reactor setup showed in diagram: 1 = HDPE waste plastic, 2= Glass reactor, 3 = Fractional distillation column, 4= 1st fraction temperature, $5 = 2^{\text{nd}}$ fraction temperature, $6 = 3^{\text{rd}}$ fraction temperature, $7 = 4^{\text{th}}$ fraction temperature, $8 = 5^{\text{th}}$ fraction temperature, 9= light gas cleaning system, 10= 1st fraction fuel collection tank, 11=2nd fraction fuel collection tank, 12=3rd fraction fuel collection tank, 13=4th fraction fuel collection tank, 14 = 5th fraction fuel collection tank, 15 = small pump, 16 = Teflon bag for light gas storage. Waste plastic used for experimental process was measured 500 gm by weight. Reactor was heated up from 100°C to up to 450°C gradually. Fractional column temperature was used for 1^{st} fraction at $40 \sim 65^{\circ}\text{C}$, 2^{nd} fractional column temperature was used $110 \sim 135^{\circ}$ C, 3^{rd} fractional column temperature was used 180 ~ 205°C, 4th fractional temperature was used 260~28 °C and finally 5th fraction temperature was used $340 \sim 365^{\circ}$ C. Main goal of this particular experiment was to collect 2nd fraction fuel. Fuel collection percentage was 29% for the 2nd collection (naphtha chemical). During fractional distillation process some light gas was generated at around 5% and solid black residue was 4% and rest of percentage other grade fuels was 62% which is demonstrated in diagram number 10, 12, 13 and 14 collection tank. Chemical production process light gas was passing (through number 9) liquid alkali solution for removing contamination and small pump was for light gas to transfer into Teflon bag. Collected chemical product purified using RCI purification unit to remove water and ash contents from the fuel. The 2nd fraction fuel density is 0.74 g/ml and fuel was transparent and fuel color was light yellow.

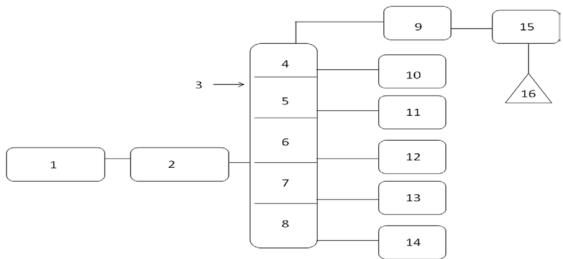


Fig. 1 HDPE waste plastic to chemical production process

III. ANALYSIS RESULTS & DISCUSSION

A. Analysis Techniques

Perkin Elmer GC/MS was used for liquid product analysis. GC/MS model number Clarus 500 and carrier gas was helium, 30 m length capillary column was used for Gas chromatography, and EI detector was used for compound mass detection. Auto sampler process was used for GC/MS analysis and sample was used only 5 μL . GC temperatures used for analysis were 40 to 325°C and rate was 10°C/min and MS mass detection was $35.00 \sim 528.00$ EI+. FT-IR spectrum 100 was used for liquid product analysis purposed and NaCl cell was used for sample holding and cell thickness was 0.25 mm, range was 4000-400 cm $^{-1}$, resolution was 4 and scene number was 32.

B. Liquid Products Analysis

By using GCMS (Model Clarus 500) analysis of HDPE waste plastic to 2nd fractional fuel or chemical product (Fig. 2 and Table 1) in accordance with retention time and trace mass indicate various types of compound are present. HDPE 2nd fraction is collected at 110°C during experiment. High intensity compounds are preferred in the analysis. An investigated carbon range in the analyzed fuel is C₄ to C₁₅ because by fractional distillation large carbon chains are breaking down into small chain, resulting in lower carbon range. Most of the peaks are considered in the analysis and as per their retention time and trace mass maximum peaks are mentioned, in accordance to retention time 1.64 and trace mass 43 derived compound is Butane (C_4H_{10}) , retention time 1.89 and trace mass 42, compound is Cyclopropane, 1, 2-dimethyl-, cis- (C_5H_{10}) , retention time 1.93, trace mass 43 compound is Cyclopropane, 1, 2dimethyl-, cis- (C₅H₁₀), retention time 2.08, trace mass 67 compound is 1, 3-Pentadiene (C₅H₈), retention time 2.34

and trace mass 42 compound is Butane, 2, 3-dimethyl- (C_6H_{14}) , retention time 2.52, trace mass 56, compound is 1-Pentene, 2-methyl- $(C_{13}H_{28})$, retention time 2.60 and trace mass 56, compound is Hexane (C_6H_{14}) , retention time 2.92 and trace mass 56, compound is Cyclopentane, methyl- (C_6H_{12}) , retention time 3.16 and trace mass 67, compound is Cyclopentene, 1-methyl-, (C₆H₁₀), retention time 3.32 and trace mass 41, compound is Cyclohexane (C₆H₁₂), retention time 3.66 and trace mass 56, compound is 2-Heptene (C_7H_{14}) , retention time 3.79 and trace mass 57, compound is Heptane (C₇H₁₆), retention time 4.10 and trace mass 41, compound is Cycloheptene (C₇H₁₂), retention time 4.33 and trace mass 69, compound is Cyclopentane, ethyl-(C₇H₁₄) etc. Also in the middle of the analysis index retention time 4.63 and trace mass 67, compound is Cyclopentane, ethylidene, (C_7H_{12}) , retention time 4.89 and trace mass 67, compound is Cyclohexene, 1-methyl-, (C₇H₁₂), retention time 5.20 and trace mass 41, compound is 2-Octene, (Z), (C₁₈H₁₆), retention time 5.27 and trace mass 55, compound is Cyclopentane, 1-ethyl-2-methyl-, cis- (C₈H₁₆), retention time 5.35 and trace mass 43, compound is Octane (C₈H₁₈), retention time 5.84 and trace mass 67, compound is 1-Methyl-2-methylenecyclohexane, (C₈H₁₄), retention time 6.02 and trace mass 83, compound is ethylcyclohexane,

 (C_8H_{16}) , retention time 6.16 and trace mass 67, compound is Cyclopentene-1-Propyl (C₈H₁₄), retention time 6.59 and trace mass 81, Cyclohexene-1-Ethyl (C₈H₁₄), retention time 7.06 and trace mass 43, compound is Nonane (C9H20), retention time 7.70 and trace mass 55 Compound is Cyclohexane, propyl- (C_9H_{18}) , retention time 8.63 and trace mass 41, compound is Decene (C10H20), retention time 8.67 and trace mass 57, compound is Decane $(C_{10}H_{22})$, retention time 10.27 and trace mass 41, compound is 1-Undecene, $(C_{11}H_{22})$, retention time 10.41 and trace mass 57, compound is Undecane (C11H24), retention time 11.83 and trace mass 41, compound is 1-Dodecane (C₁₂H₂₄), retention time 11.95 and trace mass 57, compound is Tridecane $(C_{12}H_{26})$, etc. At the end phase of the analysis index high retention time and trace mass such as retention time 13.29 and trace mass 41, compound is 1-Tridecane (C₁₃H₂₆), retention time 13.41, trace mass 57 compound is Tridecane (C₄H₁₀), retention time 14.68, trace mass 41 compound is 1-Tetradecene, retention time 14.78, trace mass compound is Tetradecane (C₁₄H₃₀), retention time 15.98, trace mass 55 compound is 1-Pentadecene and ultimately retention time 16.09, trace mass 57, compound is Pentadecane ($C_{15}H_{32}$), etc.

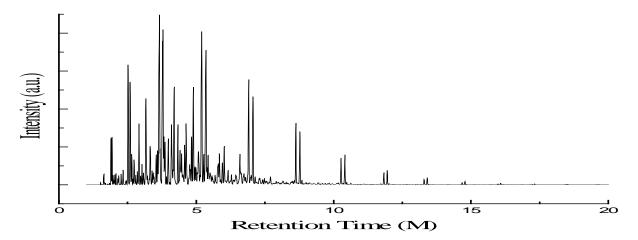


Fig. 2 GC/MS Chromatogram of HDPE waste plastic to chemical product

TABLE I GC/MS CHROMATOGRAM OF HDPE WASTEPLASTIC TO CHEMICAL PRODUCT COMPOUND LIST

Number of Peak	Retention Time (min)	Trace Mass (m/z)	Com poun d Name	Compound Formula	Mole cular Weight	CAS Number
1	1.64	43	Butane	C_4H_{10}	58	106-97-8
2	1.89	42	Cyclopropane, 1,2-dimethyl-, cis-	C_5H_{10}	70	930-18-7
3	1.93	43	Pentane	C_5H_{12}	72	109-66-0
4	2.08	67	1,3-Pentadiene C ₅ H		68	504-60-9
5	2.34	42	But ane, 2,3-dimethyl-	C_6H_{14}	86	79-29-8
6	2.52	56	1-Pentene, 2-methyl-	C_6H_{12}	84	763-29-1
7	2.60	56	Hexane	C_6H_{14}	86	110-54-3
8	2.92	56	Cyclopent ane, methyl-	C_6H_{12}	84	96-37-7
9	3.16	67	Cyclopentene, 1-methyl-	C_6H_{10}	82	693-89-0
10	3.32	41	Cyclohexane	C_6H_{12}	84	110-82-7
11	3.66	56	2-Heptene	C_7H_{14}	98	592-77-8
12	3.79	57	Heptane	$C_{7}H_{16}$	100	142-82-5
13	4.10	41	Cycloheptene	C_7H_{12}	96	628-92-2

14	4.33	69	Cyclopentane, ethyl	$C_{7}H_{14}$	98	1640-89-7
15	4.63	67	Cyclopentane, ethylidene-	C_7H_{12}	96	2146-37-4
16	4.89	67	Cyclohexene, 1-methyl-	C_7H_{12}	96	591-49-1
17	5.20	41	2-Octene, (Z)- C ₈ H ₁₆		112	7642-04-8
18	5.27	55	Cyclopentane, 1-ethyl-2-methyl-, cis-	C ₈ H ₁₆	112	930-89-2
19	5.35	43	Octane	$C_{8}H_{18}$	114	111-65-9
20	5.84	67	1-Methyl-2-methylenecyclohexane	C_8H_{14}	110	2808-75-5
21	6.02	83	Cyclohexane, ethyl-	C_8H_{16}	112	1678-91-7
22	6.16	67	Cyclopentene, 1-propyl- C ₈ H ₁₄		110	3074-61-1
23	6.59	81	Cyclohexene, 1-ethyl-	C_8H_{14}	110	1453-24-3
24	6.91	56	1-Nonene	C_9H_{18}	126	124-11-8
25	7.06	43	Nonane	C_9H_{20}	128	111-84-2
26	7.70	55	Cyclohexane, propyl-	C_9H_{18}	126	1678-92-8
27	8.63	41	1-Decene	$C_{10}H_{20}$	140	872-05-9
28	8.77	57	Decane	$C_{10}H_{22}$	142	124-18-5
29	10.27	41	1-Undecene	$C_{11}H_{22}$	154	821-95-4
30	10.41	57	Undecane	$C_{11}H_{24}$	156	1120-21-4
31	11.83	41	1-Dodecene	$C_{12}H_{24}$	168	112-41-4
32	11.95	57	Dodecane	$C_{12}H_{26}$	170	112-40-3
33	13.29	41	1-Tridecene	$C_{13}H_{26}$	182	2437-56-1
34	13.41	57	Tridecane	$C_{13}H_{28}$	184	629-50-5
35	14.68	41	1-Tetradecene	$C_{14}H_{28}$	196	1120-36-1
36	14.78	57	Tetradecane	$C_{14}H_{30}$	198	629-59-4
37	15.98	55	1-Pent adecene	$C_{15}H_{30}$	210	13360-61-7
38	16.09	57	Pentadecane	$C_{15}H_{32}$	212	629-62-9

FT-IR Spectrum-100 analysis of HDPE waste plastic to chemical product (Fig. 3 and Table 2) in favor of wave number, several types of functional groups are present. In accordance with wave number 2959.01 cm⁻¹, 2732.21 cm⁻¹ and 2669.08 cm⁻¹ functional group is C-CH₃, wave number 1822.20 cm⁻¹ and 1717.18 cm⁻¹ compound is Non-Conjugated and wave number 1642.41 cm⁻¹, functional group is Conjugated. Then wave number 1471.60 cm⁻¹, functional group is CH_2/CH_3 , wave number 1378.66 cm⁻¹, functional group is -CH₃, wave number 993.43 cm⁻¹ and 905.90 cm⁻¹, functional group is -CH=CH₂, ultimately wave number 965.22 cm⁻¹, functional group is -CH=CH-(trans) as well as wave number 726.87 cm⁻¹, 694.24 cm⁻¹ and 674.73 cm⁻¹ functional group is -CH=CH-(cis). Energy value are calculated, using formula is Energy=hv, where h=plank constant, υ=frequency of photon and υ=cW, therefore, E=hcW, where C=the speed of light (3x10¹⁰ cm/sec), W=wave number in cm⁻¹. According to equation

high wave number light has more energy than low wave number light such as wave number 2959.01 cm⁻¹ (C-CH₃), energy= $5.87X10^{-20}$ J, wave number 2732.21 cm⁻¹ (C-CH₃), energy= 5.42×10^{-20} J, wave number 2669.08 cm⁻¹ (C-CH₃), energy= 5.30×10^{-20} J, wave number 1822.20 cm⁻¹ (Non-Conjugated) energy, E=3.61X10⁻²⁰ J, wave number 1717.18 cm⁻¹ (Non-Conjugated) energy, E=3.41X10⁻²⁰ J, wave number 1641.86 cm⁻¹ (Conjugated) energy, E=3.26X10⁻²⁰ J, wave number $1471.60 \text{ cm}^{-1} (\text{CH}_2/\text{CH}_3) \text{ energy}, E = 2.92 \times 10^{-1} \text{ cm}^{-1} (\text{CH}_2/\text{CH}_3) \text{ energy}$ 20 J, wave number 1378.66 cm⁻¹ (CH₃) energy, E = 2.73X10⁻¹ 20 J, wave number 993.43 cm $^{-1}$ (-CH=CH₂) energy, $E=1.97x10^{-20} J$, wave number 965.22 cm⁻¹ (-CH=CH-(cis)) energy, $E=1.91x10^{-20} J$, wave number 905.90 cm⁻¹ (-CH=CH₂) energy, E= 1.80×10^{-20} J, wave number 726.87 cm -CH=CH- (cis), energy, E=1.44 $\times 10^{-20}$ J, wave number 694.24 cm^{-1} (-CH=CH- (cis)), energy, E=1.37 x10⁻²⁰ J and ultimately wave number 674.73 cm⁻¹ (-CH=CH- (cis)), energy, $E=1.34 \times 10^{-20} \text{ J as well.}$

TABLE II HDPE WASTEPLASTICTO HDPE WASTE PLASTIC TO CHEMICAL PRODUCT FUNCTIONAL GROUP NAME

Number of Wave	Wave Number (cm ⁻¹)	Functional Group Name	Number of Wave	Wave Number (cm ⁻¹)	Functional Group Name
1	2959.01	C-CH ₃	8	1378.66	CH ₃
2	2732.21	C-CH ₃	9	993.43	-CH=CH ₂
3	2669.08	C-CH ₃	10	965.22	-CH=CH-(trans)
4	1822.20	Non-Conjugated	11	905.90	-CH=CH ₂
5	1717.18	Non-Conjugated	12	726.87	-CH=CH-(cis)
6	1641.86	Conjugated	13	694.24	-CH=CH-(cis)
7	1471.60	CH_2 / CH_3	14	674.73	-CH=CH-(cis)

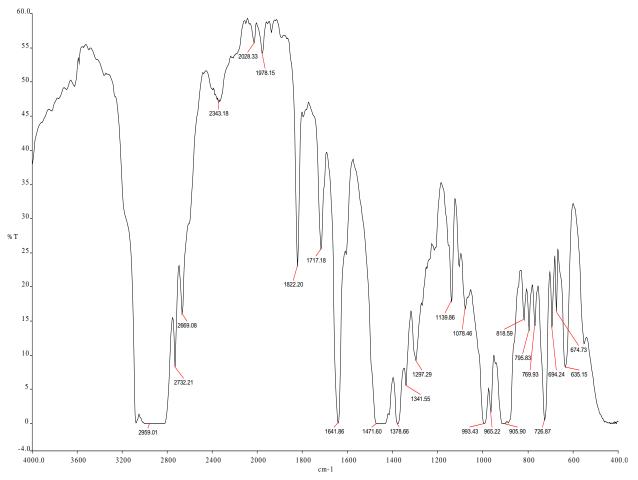


Fig. 3 FT-IR Spectrum of HDPE waste plastic to chemical product

DSC analysis of HDPE plastic to 2nd fraction fuel or chemical product (Fig. 4) indicates the onset temperature of 141.14°C. The peak temperature of the fuel is 145.80°C. Peak height is 90.7354 mW and heat flow Endo up from 100 to 95%. Peak area is 18873.444 mJ, heat enthalpy value delta H is 18873.4467 J/g. This fuel peak temperature is

145.80°C and fuel collection temperature was 110-135°C and carbon range for fuel C_4 to C_{15} . From analysis graph showed 50°C temperature fuel boil 13.87%, 92% fuel boil finished at 250°C and finally 396.69°C temperature need for whole fuel boiled because this fuel has short chain hydrocarbon C_4 to long chain hydrocarbon C_{15} .

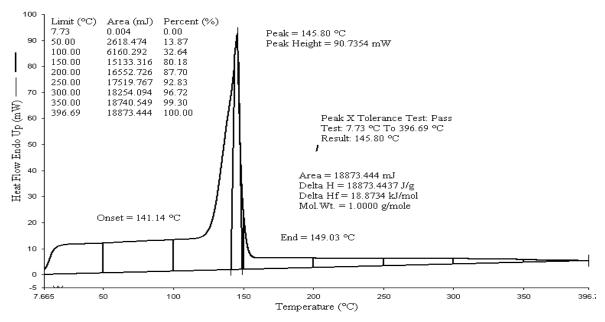


Fig. 4 DSC graph of HDPE plastic to chemical product

Some ASTM test was performed for chemical product such as n-paraffins, Iso-paraffins, Ole fins, Naphthenes, Aromatics, naphthenes and aromatics by volume (ASTM D5134_MOD), sulfur (ASTM D5453), Heat gross of combustion (ASTM D240), Density @ 15°C (ASTM D4052), API gravity @ 60°F (ASTM D4052), IBP recovery (ASTM D86), Dry vapor pressure equivalent EPA (ASTM D5191), Metal content (ASTM D5708_MOD), Appearance (ASTM D4176), Acid Number (ASTM D974), CHN Percentage (ASTM D5291), C and H ratio (ASTM D5291).

IV. CONCLUSION

Chemical product produced from HDPE waste plastic by using fractional distillation process. Temperature range was setup for particular chemical product 110-135°C. Chemical product conversion rate was good percentage from HDPE waste plastic. Analysis of chemical product result shows short to long chain aliphatic hydrocarbon mostly alkane and alkene group compounds are present. Carbon range showed from GC/MS analysis C₄ to C₁₅. By using this technology waste plastic could be removed from land fill and save the environment and support the chemical sector. GCMS (Gas

Chromatography and Mass Spectrometer) analysis of HDPE 2nd fraction fuel which is similar to naphtha or chemical product found that numerous aliphatic and aromatic compounds are available in accordance with their retention time and trace mass. In some cases appeared that at high retention time and high trace mass high peak intensity compound are appeared versus at low retention time and low trace mass low peak intensity compounds are emerged as well. GCMS analyses gave actual entirety of compounds which is present in the fuel entity. FT-IR (Fourier Transform Infra-red Spectrometer) analysis is giving the exact availability of hydrocarbon functional groups in the fuel including other organic and inorganic functional groups. In addition ASTM (American Standard and Testing Method) also performed some test in order to characterize the fuel properties. ASTM analysis makes sure and derived some alkene compounds such as paraffin's, olefins, naphthenes as well as aromatic compound constituents of naphtha or chemical products. DSC (Differential Scanning Calorimeter) represents the onset temperature of fuel products which is melting point of the products. In addition DSC analysis also provides percentage of burning contents versus temperature profile limit with consumed mJ (milli joule) as well as peak and peak heights which is compared to other chemical standard products respectively.

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Moinuddin Sarker, PhD, MCIC, is the Executive Vice President (EVP), CTO and Chief Operating Officer (COO) at the Natural State Research (NSR), Inc at Stamford, CT and the inventor of NSR's award winning technology to convert municipal waste plastics into liquid hydrocarbon fuel. He has a Ph. D. degree in Chemistry from University of

Manchester Institute of Science and Technology (UMIST), Manchester, UK (1996). He has more than 20 years of professional research experience in different universities and research organizations all over the world including the US, Canada, the Netherlands, Germany, Taiwan, Bangladesh and the UK. During his research work, he carried out research in four different synchrotron radiation sources around the world: CRCL lab. Daresbury, Warrington, Cheshire, UK (1991-1996), Synchrotron Radiation Research Center (SRRC), Hsinchu, Taiwan, R.O.C (1996-1999), Berlin Electron Storage Ring Company for Synchrotron Radiation (BESSY II) (2000) and Advance Photon Sources (APS), Chicago, USA (2001-2004). He has two patent pending and 55 research publications to his credit in pier reviewed journals and conferences. Dr. Sarker is a distinguished member of 25 professional organizations such as Society of Automobile International (SAE), American Chemical Society (ACS), American Physical Society (APS), American Institute of Chemical Engineering (AIChE), International Union of Pure and Applied Chemistry (IUPAC), Canadian Society for Chemistry (CSC), Chemical Institute of Canada (CIC), Canada and many more. Dr. Sarker has been invited speaker various conferences in around the USA and World. Dr. Sarker is the inventor of the technology and product entitles: "Method for converting waste plastics to lower molecular weight hydrocarbons, particularly hydrocarbon fuel materials and the hydrocarbon material produced thereby" (US and International Patent Pending). Dr. Sarker also heads a humanitarian effort in Bangladesh, the Moinuddin Foundation (www.moinuddinfoundation.org) which helps provide essentials for the poor and underprivileged.



Mohammad Mamunor Rashid born 1976 into Bangladesh and now he becomes USA citizen. He finished his M. Sc degree in Chemistry from Jagonnath University College under National University in Bangladesh. He revived his B. Sc and M. Sc degree 2000 and 2002. He is working now Natural State Research, Inc. since 2006 as

Plant Manager waste plastic to fuel conversion process and save the environment field. He is co-author of several publications about waste plastic to fuel related journal. He has almost 35 publications into various journals. He has participated seminar and conference. E-mail address: mamun@naturalstateresearch.com



Muhammad Sadikur Rahman, from Bangladesh, Permanent Resident of USA, lives in New York. He obtained his B. Sc (Hon's) 2001, M. Sc in Chemistry 2003 from M.C College under National University of Bangladesh. He has been working in the research and development field as a laboratory

Chemist in the company of Natural State Research, Inc. He is coauthor of several publications about waste plastic to fuel related journal. He has almost 15 publications into various journals. He has participated seminar and conference. E-mail address: sadik@naturalstateresearch.com



Mohammed Molla, he born 1986 into Bangladesh and now he is USA Citizen. He is studying B. Sc at City College of NY under CUNY. He is working Natural State Research, Inc as an Intern. He is co-author of several publications about waste plastic to fuel related journal. He has almost 20 publications into

various journals. He has participated seminar and conference. E-mail address: mmolla@naturalstateresearch.com