(19) World Intellectual Property Organization

International Bureau



(43) International Publication Date 13 October 2005 (13.10.2005)

PCT

(10) International Publication Number $WO\ 2005/094990\ A1$

(51) International Patent Classification⁷: 29/08, C10G 1/00, 1/10

B01J 29/06,

(21) International Application Number:

PCT/IN2004/000366

(22) International Filing Date:

25 November 2004 (25.11.2004)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

384/Mum/2004

30 March 2004 (30.03.2004) IN

- (71) Applicant (for all designated States except US): INDIAN OIL CORPORATION LIMITED [IN/IN]; G-9, Ali Yavar Jung Marg, Bandra (East), Mumbai 400051, Maharashtra (IN).
- (71) Applicant and
- (72) Inventor: ZADGAONKAR, Umesh [IN/IN]; 9 Buty Layout, Laxminagar, Nagpur 440022, Maharashtra (IN).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): ARORA, Ajay, Kumar [IN/IN]; c/o Indian Oil Corporation Limited, G-9 Ali Yavar Jung Marg, Bandra (East), Mumbai 400051, Maharashtra (IN). SARKAR, Biswanath [IN/IN]; c/o Indian Oil Corporation Limited, G-9 Ali Yavar Jung Marg, Bandra (East), Mumbai 400051, Maharashtra (IN). PARKASH, Shanti [IN/IN]; c/o Indian Oil Corporation Limited, G-9 Ali Yavar Jung Marg, Bandra (East), Mumbai 400051, Maharashtra (IN). SWAMI, Krishan, Kumar [IN/IN]; c/o Indian Oil Corporation Limited, G-9 Ali Yavar Jung Marg, Bandra (East), Mumbai 400051, Maharashtra (IN). SARIN, Rakesh [IN/IN]; c/o Indian Oil Corporation Limited, G-9 Ali Yavar Jung Marg, Bandra (East), Mumbai 400051, Maharashtra (IN). KRISHNAN, Venkatachalam [IN/IN]; c/o Indian Oil Corporation Limited, G-9 Ali Yavar Jung Marg, Bandra (East), Mumbai 400051, Maharashtra (IN). MAKHIJA, Satish [IN/IN]; c/o Indian Oil Corporation Limited, G-9 Ali Yavar Jung Marg, Bandra (East), Mumbai 400051, Maharashtra (IN). VERMA, Ram, Prakash [IN/IN]; c/o Indian Oil Corporation Limited, G-9 Ali Yavar Jung Marg, Bandra (East), Mumbai 400051, Maharashtra (IN). GHOSH, Sobhan [IN/IN]; c/o Indian Oil Corporation Limited, G-9

Ali Yavar Jung Marg, Bandra (East), Mumbai 400051, Maharashtra (IN). **RAJE, Niranjan, Raghunath** [IN/IN]; c/o Indian Oil Corporation Limited, G-9 Ali Yavar Jung Marg, Bandra (East), Mumbai 400051, Maharashtra (IN). **ZADGAONKAR, Alka, Umesh** [IN/IN]; 9 Buty Layout, Laxminagar, Nagpur, Maharashtra 440022 (IN).

- (74) Agents: ANAND, Pravin et al.; Anand And Anand Advocates, B-41 Nizamuddin East, New Delhi 110013 (IN).
- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to the identity of the inventor (Rule 4.17(i)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)
- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE,

[Continued on next page]

(54) Title: A CATALYST COMPOSITION FOR CATALYTIC CRACKING OF WASTE PLASTIC

(57) Abstract: The present invention relates to a process of preparing a catalytic cracking catalyst comprising: - mixing the following ingredients in the proportion indicated there against faujasite zeolite - 5-35 wt %; pseudoboehmite alumina - 10-40 wt %; polyammonium silicate - 1-10 wt %; kaolin clay - 15-60wt %; - milling said ingredients and making a slurry using water, - spray drying said slurry to micro-spheres, and - calcining said micro-spheres at 500° C for 1 hour to obtain the catalyst.



WO 2005/094990 A1



EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)

— of inventorship (Rule 4.17(iv)) for US only

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

5 TITLE OF THE INVENTION

A Catalyst Composition For Catalytic Cracking Of Waste Plastic. Field of Invention

The present invention relates to a process of preparing catalytic cracking catalyst for use in catalytic cracking waste plastic.

10 Background of the Invention

15

20

25

30

Plastic is widely used in all kinds of products in the industry and our daily life and in considerable quantities because of its numerous advantages such as being cheap, light easily shaped and water resisting. Polyethylene, polypropylene, polyvinylchloride, polystyrene are few examples of these polymeric plastic materials. Therefore, plastic waste has become a major element in garbage. However, because most of the plastic waste does not decompose naturally in garbage dumps and creates toxic smoke after burning, it is not environment friendly and causes very serious environmental problems. It is well known that these plastic polymers are not biodegradable and needs to be recycled. However, recycling of plastic waste deteriorates the quality of materials and this waste has to be taken care of as per environmental regulations.

Recycling of plastic waste into other plastic products is a useful way to reduce the plastic waste, but this method is limited to thermoplastic materials and the recycled plastic product is of poor quality so that the recycling is not an efficient way to handle all plastic waste. The plastic waste could be containing polyethylene, polypropylene, polyvinyl chloride, polyvinylidene chloride, ABS resin, polyvinyl alcohol, polycarbonate, polyester resin or polyamide. The pyrolysis of plastic waste could lead to the formation of a mixture of hydrocarbons like paraffin and olefin. The pyrolysis of polyvinyl chloride plastic can lead to the formation of toxic emission such as polychlorinated dibenzodioxins (PCDD), dibenzofurans (PCDF) and polychloro biphenyls (PCB) along with highly corrosive hydrochloric acid.

5

10

15

20

25

30

Almost all plastic waste is dumped on land reclamation sites. Alternatively burning of plastic has been tried. In the case of dumping of plastic waste on a reclaimed land, it is difficult to secure a land. In the case of burning of plastic waste, these are reports of damage to the incinerator. Burning process also gives off poisonous gases and a foul odour during the incineration.

In this a context, attempts have been made in recent years to develop a method for recycling and reusing of plastic waste without pollution and for effectively utilizing the recycled plastic as resources.

US Patent Application No. 2002/0006367 claims a method for conversion of plastic waste into oil by a reaction using water in a super critical or near super critical form as a reaction medium. US Patent Application No. 2003/0019789 claims to development of method of conversion of waste plastic material into gasoline, kerosene and diesel oil fractions. In another US Patent Application 2002/0156332, a method has been invented for cracking of waste plastic to obtain partly gasoline, partly liquid hydrocarbon and remaining residues.

US Patent No. 5226926 has claimed the method of simultaneous treatment of waste plastic and spent vegetable oil by heating and shaping the resultant mixture into a solid fuel product. EP Patent Application 0636674 discloses a thermal decomposition apparatus for plastic treatment. Plastics are melted and thermally decomposed and the resulting decomposition gas is cooled for condensation and received in form of thermal decomposition fuel. A method of conversion of plastic including PVC into oil by thermal decomposition is also claimed in US Patent No. 5597451. EP Patent No. 1101812 provides a process for getting oily fraction from waste plastic waste.

Besides above examples of conversion of waste plastic to hydrocarbon mixture, attempts have been made to invent process of production of value added chemicals. US Patent No. 5639937 claims for a process for the production of ethylene, propylene or C₄ olefin or their mixtures from waste plastics. US Patent 4515659 has claimed a process for pyrolytic conversion of

waste plastic and waste rubber to olefinic hydrocarbon. US Patent No. 4429172 claims a process for the production of modified pitches and low boiling aromatics and olefins by thermal treatment of plastic waste.

A process for a making of high VI lubricating oil composition from mixture of waste plastics through the steps of pyrolysis, hydro-treating and catalytic dewaxing has been claimed in US Patent No. 6150577. In another invention, plastic waste has been converted to high VI lubricating oil composition with additional step of dimerization, as claimed in US Patent No. 6288296.

10

15

20

25

30

The above-cited patents cover a wide spectrum of manufacture of hydrocarbon mixtures, from ethylene, propylene to lubricating oils and aromatic pitches. Waste plastics, that are polymer of high molecular weight, have a problem that on simple thermal decomposition they produce mainly waxy distillates with little or no production of gasoline, kerosene, light oils etc.

It would be advantageous to have a process for conversion of readily available waste plastic to selectively produce olefins (C_4 to C_{25}) using zeolite based acid catalyst, which can be utilized as raw material for synthesis of synthetic lubricants like PAO & linear alkyl benzenes etc. and could be used as liquid fuel. Further more catalytic treatment is carried out in such a way that chlorine present in the feed material is predominantly or completely eliminated as HCl.

OBJECTS AND SUMMARY OF THE INVENTION:

The object of the present invention is to provide a process for preparing a catalytic cracking catalyst for conversion of waste plastic to higher olefins (C_4 to C_{25}).

To achieve the aforementioned objects, the present invention provides a process of preparing a catalytic cracking catalyst comprising:

- mixing the following ingredients in the proportion indicated there against

faujasite zeolite

5-35 wt %

pseudoboehmite alumina - 10-40 wt % polyammonium silicate - 1-10 wt % kaolin clay - 15-60wt %

- milling said ingredients and making a slurry using water,
- spray drying said slurry to micro-spheres, and
- calcining said micro-spheres at 500°C for 1 hour to obtain the catalyst

Water used is a demineralized water.

15

25

30

The said ingredients are in the following proportion:

Faujasite zeolite - 15-30 wt %

Pseudoboehmite alumina - 20-40 wt %

Polyammonium silicate - 1-10 wt %

Kaolin clay - 40-60wt %

The present invention also provides a catalytic cracking catalyst whenever prepared by the above process .

A process of catalytic cracking waste plastics using the catalyst comprises:

- cleaning, shredding and cutting waste plastics into at least 1x1 mm pieces,
- mixing said plastic waste pieces with 2-10 % by wt of said catalyst,
- cracking said mixture of plastic water pieces and catalyst at 300 to 400°C under atmospheric pressure to obtain a mixture of C₄-C₂₅ olefins.

The waste plastics contain either polyethylene, polypropylene, polyvinyl chloride, polystyrene, polyethylene, terphthalate, polymide and mixture thereof

The percentage of catalyst used in the catalytic cracking of plastic waste varies with respect to the plastic waste cracked.

5 DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a process for conversion of readily available waste plastic to selectively produce olefins (C_4 to C_{25}) using indigenously developed zeolite based acid catalyst

C₄ - C₂₅ polyolefins are used for the synthesis of synthetic hydrocarbon products like polypalphaolefin, linear alkyl benzene. These synthetic lubricants exhibit lower friction characteristics and are used in various types of equipment including auto-engine, transmission, worm gears and traction-devices. The superiority in terms of appropriate viscosity over wide temperature range, low pour point, high oxidative and thermal stability is well established than natural mineral oils. However, the cost of α-olefins monomers has been major constraints in the commercialization of synthetic lubricant.

The search efforts are directed towards development of new sources of α -olefins. US Patent No. 5847209 claims to a process for the separation of olefins and paraffins from the paraffin-olefin mixture by formation of urea adduct refinery petroleum streams. US Patent No. 6184429 has utilized the separated olefin mixture for the synthesis of olefin oligomers.

There are claims for production of lower olefins by the pyrolysis plastic waste as in US Patent 5639937. In accordance with the objects of the present invention, to optimize the pyrolytic catalyst and reaction conditions to get preferably higher olefins of carbon C₈-C₁₄, the raw materials for this process is usual urban and industrial waste plastic which contains PP, PE, PVC, PET, PS etc. type of plastic. This waste plastic is treated with an indigenously developed solid acidic catalyst at 300-400 °C. The catalyst to feed wt ratio is 1-10 % and heating rate is optimized in order to get preferentially higher olefins.

30 Catalyst:

10

15

20

25

The Zeolite Component

The zeolite used may be any derivatives of faujasite, like NaNH₄. Y, ReNH_{.4} Y. Preferably, USY zeolite is employed having high hydrothermal

stability, with S_i O₂/Al₂ O₃ ratio of 6.5-8.0. The sodium content present in USY zeolite is preferred to be less than 1% wt. Further, to avoid post preparation rare-earth exchanged step, it is preferred to use rare-earth exchanged USY zeolite. Rare earth source may be single rare-earth chloride or a mixture of rare-earth chlorides (of La, Ce, Nd, Pr).

To obtain the rare earth form of USY zeolite, low soda USY zeolite is dispersed in rare-earth chloride solution at elevated temperature of 60-80.degree. C. for a period of 20-40 minutes. On completion of exchange, the final product is washed free of chlorides, which on volatile free basis contained 3.8-4% wt. of Re₂ O₃ and about 0.9% wt of Na.

The Pseudoboehmite Component

10

15

20

25

30

Preferably, binder grade/pseudoboehmite is used having high crystallinity and crystallite size in the range of 45-60 A^0 and having low sodium content, preferably less than 0.1% wt. The alumina is preferred to have good surface area of 200-300 m^2 /g. The pseudoboehmite alumina with the above properties is required to be gelled by a suitable acid, mineral or organic. Organic acids are preferred in place of mineral acids as chloride, sulfate, and nitrate radicals present in the latter are hazardous to hardware as well as to environment. Gelling character of alumina depends on nature of acid, quantity, and temperature. We have found that in order to obtain an alumina suitable to bind zeolite and clay and make the slurry pumpable, balanced quantity of acid must be used and gelled under controlled conditions. Alumina used in the present investigation has surface area of 260 m^2 /g, crystallite size of 55 A^0 pore radius of 28 A^0 .

The Polysilicate Component

Polysilicate, either Na stabilized or NH₄ stabilized with low soda content is referred for use in the catalyst of our invention. NH₄ stabilized polysilicate is more preferred than the Na stabilized polysilicate, for the reason of lower sodium level. This ingredient, due to its free flow nature and availability in low soda form, is ideal for creating low acidic matrix in the catalyst in the presence

of alumina. Polysilicate with small particle size of 180-250 A⁰ is preferred for incorporation into the catalyst of our invention. Ammonium polysilicate with 16% SiO₂ content and average particle size of 220 A⁰ is used in the present investigation.

The Clay Component

10

15

20

25

30

Clays are used in cracking catalysts as filler, for improving the density and dissipation of heat. The most commonly used clays are kaolinite and halloysite. They have a two-layer structure consisting of alternating sheets of SiO₄tetra- hedra and AlO₆octahedra. Other clays like montmorillonite, bentonites, etc., have also been cited as substitutes for fillers. Clays for the application of catalyst formations are required to be purified and have average particle size of about 2 microns or less. The clay, which is used in the present investigation, is of kaolinite type with more than 80 % fractions below 2 microns and sodium content of less than 0.3 wt %.

The zeolite component present in the catalyst composite is in the range of 5-35 wt %, a preferred range being from 15-30 wt %, modified alumina is in the range of 10-40 wt %, a preferred range being 20-30 wt %. Kaolin clay is present in the range of 40-60-wt %, the preferred range being 45-55 wt %. The residual soda level in the finished catalyst is in the range of 0.2-0.7 wt %, preferred level being less than 0.5 wt %. The rare earth oxide content in the catalyst is in the range of 0.5-2 wt %., the preferred range being 0.8-1.2 wt %. The rare earth metal salts employed can either be the salt of a single rare earth metal or mixture of rare earth metals, such as chlorides consisting essentially of Lanthanum, Cerium, Neodymium with minor amounts of Samarium, Gadolinium, and Yttrium.

The features described in the foregoing description and in the following may, both separately and in any combination thereof, be material for realizing this invention in diverse forms thereof.

The present invention is further described in the following examples, which, however, is not to be construed as limiting. The results are shown in Table I

EXAMPLE-1

10

15

20

25

30

This example describes the process for the preparation of modified alumina with silica. 38 gm of formic acid (85 wt % concentration, LR grade, M/s SD Fine Chemicals, India) was diluted with 750 g of DM water. To this diluted acid, 214 g of alumina was added (Pural SB grade with 24 wt % moisture from M/s. Condea, Germany) under stirring. After thorough dispersion of alumina, the mixture was held for 24 hrs at 40 °C. The viscous alumina product with a pH of 2.5-2.75 was then reacted with 156 g of Ammonium Polysilicate (16 wt% SiO2, from M/s Bee Chems, Kanpur, India) and was ready for use.

EXAMPLE-2

This example illustrates the process for preparation of rare earth exchanged USY zeolite. 300 g commercial USY zeolite (with 11 wt % moisture, 1.35 wt % Na, 86% crystallinity, from M/s PQ Corporation, USA) was dispersed in 1 wt % rare earth chloride solution, maintaining solid-liquid ratio of 1:10 at a temperature of 60 °C. C. After exchanging for 20 minutes, zeolite was washed chloride free and dried at 110 °C, for 16 hours to obtain rare earth exchanged ammonium Y zeolite. The product contains 4 wt %, ReO, 0.9 wt% Na.

EXAMPLE-3

This example describes the process for preparation of catalyst using rare earth exchanged USY zeolite prepared as per example 2, non-modified alumina, ammonium polysilicate, and kaolin clay. Slurry with pH of 3.5 and solid content of 28 wt% was prepared, having the following composition (wt %): zeolite 25, alumina 30, kaolin clay 40 and silica 5.

214 g of alumina was reacted with 17.25 g of formic acid at room temperature (20 °C.). To the alumina, 156 g of ammonium polysilicate and 253 g of kaolin clay (with 15 wt % moisture from M/s Kerala Ceramics, Kundera, India) were added. 166.5 g rare earth exchanged USY zeolite (11 wt % moisture) was made into a fine paste by milling with 170 g DM water. The final slurry was milled thoroughly and spray dried at inlet temperature 330 °C, outlet temperature 140 °C, and feed rate of 100 g/minute. The spray-dried micro spheres were calcined at 500 °C. for one hour to obtain final catalyst.

EXAMPLE-4

5

10

15

This example illustrates a process of preparing catalyst as per Example 3 with the exception that modified aluminum silica composite prepared as per example 1 of this invention was used. The product was calcined and steam deactivated.

EXAMPLE-5

Faujasite zeolite, pseudoboehmite, alumina, polyammonium silicate and kaolin clay are combined in particular ratios to get the finished catalyst. Preferably the content of Faujasite zeolite is about 5 to 35 %,the content of pseudoboehmite, alumina is about 10 to 40 wt %, the content of polyammonium silicate is about 1 to 10 % wt and the content of the kaolin clay is about 1-60 wt%.

25 EXAMPLE-6

30

This example illustrates a process of preparing catalyst Faujasite zeolite, pseudoboehmite, alumina, polyammonium silicate and kaolin clay are combined in particular ratios to get the finished catalyst. Preferably the content of Faujasite zeolite is about 25 %, the content of pseudoboehmite, alumina is about 30 wt %, the content of polyammonium silicate is about 5% wt and the content of the kaolin clay is about 40wt%.

5

10

15

20

25

30

EXAMPLE-7

The thermal cracking of polystyrene predominant plastic, which was cleaned, shredded and cut into 1 X 1 mm pieces was carried out in a catalytic reactor. The cracking is carried out under atmospheric pressure and at a temperature range of 300-400°C. The catalyst used is an indigenously developed zeolite based acidic catalyst, which is used in the ratio of 3 wt% of the plastic taken. The resulting gaseous hydrocarbons are passed through column of calcium oxide to make it chlorine free gaseous hydrocarbons. The wt% distillate obtained is in the range of 70-90 wt% by weight of the starting material taken. Gas chromatography shows the distillate to be predominantly C_6 - C_9 olefins. The residual left over in the catalytic reactor is mixed with equal amount of non – edible vegetable oil and heated to temperature range of 100-120° C and then discharged from the residual discharging portion of the reactor.

EXAMPLE-8

The polypropylene predominant plastic was cleaned in pieces as in example-1. The plastic was premixed with 3.5wt% of catalyst and charged into pyrolysis reactor. The reactor was heated to temperature range of 320-360° C. The resulting gaseous hydrocarbons were made chlorine free by passing through calcium oxide. The residual left over was discharged from residual discharging portion, which was mixed with non-edible oil to be used as solid fuel bricks. The distillates obtained are 60=70 % by weight of the initial plastic taken. The distillates contain predominantly C₆-C₈ olefins.

EXAMPLE -9

The polyethylene predominant plastic was cleaned, shredded and cut into pieces of the size 1mm X 1mm, the plastic product was premixed with 2 wt% catalyst and heated up in the pyrolysis reactor. The temperature range being 320-380°C. The distillate obtained was in the region of 55-65 wt% of the plastic taken. The gas chromatography analysis showed presence of predominantly C₆-C₇ olefins in the distillate.

5 EXAMPLE –10

The cracking of high density polyethylene, which was cleaned, shredded and cut into 1 X 1 mm pieces was carried out in a catalytic reactor. The cracking is carried out under atmospheric pressure and at a temperature range of 300-350°C. The catalyst used is an indigenously developed zeolite based acidic catalyst, which is used in the ratio of 4 wt% of the plastic taken. The resulting gaseous hydrocarbons are passed through column of calcium oxide to make it chlorine free gaseous hydrocarbons. The wt% distillate obtained is in the range of 80-90 wt% by weight of the starting material taken. Gas chromatography shows the distillate to be predominantly C₆-C₉ olefins.

15 EXAMPLE-11

10

20

25

30

The PVC containing plastic was cleaned and cut into 1 mm X 1mm pieces. These pieces were injected in a pyrolysis reactor and 8 wt% of catalyst was used. The temperature range being in the region of 320-360 $^{\circ}$ C. The resulting gaseous hydrocarbons are passed through column containing calcium oxide in order to make it chlorine free. The percentage of distillate obtained is in range of 50-70 wt% of the initial weight of plastic taken. The gas chromatography analysis shows the distillate containing predominantly C_6, C_9, C_{13}, C_{18} and overall range being C_4 - C_{25} .

EXAMPLE-12

The polyethylene terphthalate predominant plastic was cleaned and cut into 1 mm X 1mm pieces. These pieces were injected in a pyrolysis reactor and 4wt% of catalyst was used. The temperature range being in the region of 300-340 $^{\circ}\text{C}$. The resulting gaseous hydrocarbons are passed through column containing calcium oxide or it's aqueous solution in order to make it chlorine free. The percentage of distillate obtained is in range of 70-80 wt% of the initial weight of plastic taken. The gas chromatography analysis shows the distillate containing predominantly $\text{C}_6\text{-C}_{10}$ and overall range being $\text{C}_4\text{-C}_{25}$.

EXAMPLE-13

The thermal cracking of polyamide (nylon) predominant plastic, which was cleaned, shredded and cut into 1 X 1 mm pieces was carried out in a catalytic reactor. The cracking is carried out under atmospheric pressure and at a temperature range of 350-400°C. The catalyst used is an indigenously developed zeolite based acidic catalyst, which is used in the ratio of 8 wt% of the plastic taken. The resulting gaseous hydrocarbons are passed through column of calcium oxide to make it chlorine free gaseous hydrocarbons. The wt% distillate obtained is in the range of 70-90 wt% by weight of the starting material taken. Gas chromatography shows the distillate to be predominantly C_{13} - C_{18} olefins. The residual left over in the catalytic reactor is mixed with equal amount of non –edible vegetable oil and heated to temperature range of 100-120°C and then discharged from the residual discharging portion of the reactor.

EXAMPLE-14

5

10

15

20

25

30

The cracking of assorted municipal plastic, which was cleaned, shredded and cut into 1 X 1 mm pieces, was carried out in a catalytic reactor. The cracking is carried out under atmospheric pressure and at a temperature range of $300\text{-}350^{\circ}\text{C}$. The catalyst used is an indigenously developed zeolite based acidic catalyst, which is used in the ratio of 2 wt% of the plastic taken. The resulting gaseous hydrocarbons are passed through column of calcium oxide or it's aqueous solution to make it chlorine free gaseous hydrocarbons. The wt% distillate obtained is in the range of 65-70 wt% by weight of the starting material taken. Gas chromatography shows the $C_4\text{-}C_{25}$ distillate to be predominantly $C_6\text{-}C_{10}$ olefins. The residual left over in the catalytic reactor is mixed with equal amount of non–edible vegetable oil and heated to temperature range of $100\text{-}120^{\circ}$ C and then discharged from the residual discharging portion of the reactor.

EXAMPLE-15

Similar to example-14 the cracking of assorted municipal plastic is carried out under atmospheric pressure and at a temperature range of 300-

330°C. The catalyst used is an indigenously developed zeolite based acidic catalyst, which is used in the ratio of 4 wt% of the plastic taken. The resulting gaseous hydrocarbons are passed through column of calcium oxide or it's aqueous solution to make it chlorine free gaseous hydrocarbons. The wt% distillate obtained is in the range of 70-80 wt% by weight of the starting material taken. Gas chromatography shows the distillate to be range of C₆-C₁₈, predominantly C₆-C₈ olefins.

EXAMPLE-16

15

An experiment was repeated for the assorted municipal plastic under reaction conditions as for EXAMPLE-15 but without the catalyst. It was found that 30-40 wt% of distillate containing mixture of olefins were obtained and a substantial amount of solid residue was left over.

5 <u>Title: Product profile from catalytic cracking of waste plastic</u> Table I

| S. | Wt. and nature of | Cataly | Temperature | Product composition |
|-----|--------------------|--------|-------------|---------------------|
| No. | plastic | st% | | |
| 1 | 50 g | 3 | 320°C | C4-C10 range |
| | polystyrene | | | C6-C9 Major |
| 2 | 50 g | 3.5 | 300-320°C | C6-C13 range |
| ! | polypropylene | | | C6-C8 Major |
| 3 | 50 g | 2 | 300°C | C4-C13 range |
| | polyethylene | | | C6-C7 Major |
| 4 | 50g | 4 | 340°C | C6-C13 range |
| | high density | | | C6-C8 Major |
| | polyethylene | | | |
| 5 | 50 g | 8 | 340°C | C4-C25 range |
| | polyvinyl chloride | | | C6-major |
| | | | | C13-18 major |
| 6 | 50 g | 4 | 300°C | C4-C25 range |
| | polyethylene | | | C6-C10 |
| | terphthalate | | | Major |
| 7 | 50 g | 9 | 375°C | C4-C25 range |
| | polyamide | | | C13-18 major |
| | (nylon) | | | |
| 8 | 50 g | 2 | 350°C | C4-C25 range |
| | plastic | | | C6-10 major |
| | mixture** | | | |
| 9 | 50 g | 4 | 330°C | C4-C18 range |
| - | plastic | | | C6-8 major |
| | mixture** | | - | |

5 **Plastic mixture generally contains 3-5wt% PVC, 5-15 wt% PET, 20-35 wt% PP, 30-50 wt% PE, 5-10 wt% nylon etc.

5 We claim:

1. A process of preparing a catalytic cracking catalyst comprising:

- mixing the following ingredients in the proportion indicated there against

faujasite zeolite - 5-35 wt %

pseudoboehmite alumina - 10-40 wt %

polyammonium silicate - 1-10 wt %

kaolin clay - 15-60wt %

milling said ingredients and making a slurry using water,

- spray drying said slurry to micro-spheres, and

- calcining said micro-spheres at 500°C for 1 hour to obtain the catalyst

- 2. A process as claimed in claim 1 wherein water used is a demineralized water.
- 20 3. A process as claimed in any one of the preceding claims wherein said ingredients are in the following proportion

Faujasite zeolite - 15-30 wt %

Pseudoboehmite alumina - 20-40 wt %

Polyammonium silicate - 1-10 wt %

25 Kaolin clay - 40-60wt %

- 4. A catalytic cracking catalyst whenever prepared by the process as claimed in claim 1 to 3.
- 5. A process of catalytic cracking waste plastics using the catalyst as claimed in the preceding claims comprising:
- cleaning, shredding and cutting waste plastics into at least 1x1 mm pieces,
 - mixing said plastic waste pieces with 2-10 % by wt of said catalyst,

cracking said mixture of plastic water pieces and catalyst at 300 to 400° C under atmospheric pressure to obtain a mixture of C₄-C₂₅ olefins.

6. A process as claimed in claim 3 wherein waste plastics contain either polyethylene, polypropylene, polyvinyl chloride, polystyrene, polyethylene, terphthalate, polymide and mixture thereof.

10

7. A process as claimed in claim 3 wherein the percentage of catalyst used in the catalytic cracking of plastic waste varies with respect to the plastic waste cracked.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/IN04/00366

| A. CLASSIFICATION OF SUBJECT MATTER IPC(7) : B01J 29/06, 29/08; C10G 1/00, 1/10 | | | | | | | |
|---------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|--|--|--|--|
| US CL: 502/64, 68, 79; 585/240, 241 According to International Patent Classification (IPC) or to both national classification and IPC | | | | | | | |
| B. FIELDS SEARCHED | | | | | | | |
| Minimum documentation searched (classification system followed by classification symbols) | | | | | | | |
| U.S.: 502/64, 68, 79; 585/240, 241 | | | | | | | |
| Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched | | | | | | | |
| Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) | | | | | | | |
| C. DOC | C. DOCUMENTS CONSIDERED TO BE RELEVANT | | | | | | |
| Category * | Citation of document, with indication, where a | | Relevant to claim No. | | | | |
| X | US 6,114,267 A (GHOSH et al) 05 September 2000 | 1-4 | | | | | |
| A | | 5-7 | | | | | |
| X | US 5,443,716 A (ANDERSON et al) 22 August 199 | 5 (22.08.1995), columns 4-9. | 4-7 | | | | |
| A | | | 1-3 | | | | |
| Α | US 5,744,668 A (ZHOU et al) 28 April 1998 (28.04 | 1-7 | | | | | |
| | | | | | | | |
| Further | documents are listed in the continuation of Box C. | See patent family annex. | | | | | |
| * S | pecial categories of cited documents: | "T" later document published after the inter date and not in conflict with the applica | | | | | |
| | defining the general state of the art which is not considered to be lar relevance | principle or theory underlying the inven | ntion | | | | |
| "E" earlier ap | plication or patent published on or after the international filing date | "X" document of particular relevance; the considered novel or cannot be consider when the document is taken alone | | | | | |
| establish specified) | | "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination | | | | | |
| "O" document | referring to an oral disclosure, use, exhibition or other means | being obvious to a person skilled in the | art | | | | |
| | published prior to the international filing date but later than the ate claimed | "&" document member of the same patent f | | | | | |
| | ctual completion of the international search | Date of mailing of the international searce | h report F | | | | |
| 27 July 2005 | (27.07.2005) ailing address of the ISA/US | Authorized officer | , and a w | | | | |
| | il Stop PCT, Atm: ISA/US | | | | | | |
| Con | nmissioner for Patents | Christina Johnson DEBORAH A. THOMAS | | | | | |
| Ale | o. Box 1450 xandria, Virginia 22313-1450 o. (703) 305-3230 | Telephone No. (703) 308-06 PARALEGAL SPECIALIST GROUP-1365 | | | | | |