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(71) Applicant: **MOBIL OIL CORPORATION**
150 East 42nd Street
New York New York 10017 (US)

Director-General of the Agency of Industrial Science and Technology
Ministry of International Trade & Industry 3-1
Kasumigaseki 1-chome
Chiyoda-ku Tokyo 100 (JP)

RESEARCH DEVELOPMENT CORPORATION OF JAPAN
1-18, 1-chome Akasaka
Minato-ku Tokyo (JP)

K.K. FUJI TECH
88 Uekino Yasutomi-Cho
Shiso-Gun Hyogo Prefecture (JP)

(72) Inventor: **Saito, Kiyoshi The Government Ind. Dev. Laboratory**
Hokkaido, No. 2-1, 17-chome Higashi 2-jo Tsukisamu
Toyohira-ku Sapporo City Hokkaido (JP)

Fukuda, Takashi The Government Ind. Dev.Laboratory
Hokkaido No. 2-1, 17-chome Higashi 2-jo Tsukisamu
Toyohira-ku Sapporo City Hokkaido (JP)

Suzuki, Satoru The Government Ind. Dev. Laboratory
Hokkaido No. 2-1, 17-chome Higashi 2-jo Tsukisamu
Toyohira-ku Sapporo City Hokkaido (JP)

Sato, Hideo
No. 741-1, Ohaza Kawanami Kannabe-cho
Fukayasu-gun Hiroshima Prefecture (JP)

Hirota, Toshio
No. 791-51, Kanagaya Asahi-ku
Yokohama City (JP)

(74) Representative: **Colmer, Stephen Gary**
Patent Department c/o Mobil Services Company Limited
Mobil Court 3 Clements Inn
London WC2A 2EB (GB)

(54) Process for preparing a normally liquid hydrocarbon product from plastics material.

(57) In a process for preparing a normally liquid hydrocarbon product from plastics material, particularly plastics scrap, the plastic material is thermally cracked in the molten liquid phase and the vaporous product thereby generated is catalytically converted by contact with a zeolite having a constraint index of 1-12.

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Description

PROCESS FOR PREPARING A NORMALLY LIQUID HYDROCARBON PRODUCT FROM PLASTICS MATERIAL

The present invention relates to a process for preparing from a plastics material a normally liquid hydrocarbon product which is useful, into alia, as a raw material for the production of gasoline.

As the quantity of plastics manufactured has grown in recent years, disposal of plastics scrap has become an increasing problem. Moreover, although various thermal cracking methods have been proposed as potential solutions to the disposal problem, they are disadvantageous in that formation of a considerable amount of coke and waxy materials, which tend to adhere to the inner wall of the reaction vessel, is unavoidable. Accordingly, it has not been feasible to put these methods to practical use in the disposal of commonly used plastics.

The present invention resides in a process for preparing a normally liquid hydrocarbon product, that is comprising C_5-C_{22} hydrocarbons, which comprises thermally cracking a plastics material in the molten liquid phase and catalytically converting the vaporous product thus generated in a bed containing a zeolite having a constraint index between 1 and 12.

The plastics maerial used in the process of the invention may be any polymer or copolymer of an ethylenically unsaturated monomer, including aromatic species such as polystyrene and polyethylene terephthalate, although halogen - containing polymers and copolymers should be avoided. Preferably, the material is a polyolefinic plastics material, especially polyethylene, polypropylene and polybutylene (including copolymers and mixtures containing the same as an essential component). Since the present process is specifically intended for the disposal of scrap plastics, the plastics material employed may take a wide variety of forms, such as, films, sheets, and moldings, although films and sheets are preferred. These materials, after being pulverized by appropriate means, are fed continuously to a thermal cracking reactor by means of an extruder while being heated to a liquid and molten state.

The thermal cracking step of the process of the inventon is conducted with the plastics material in the molten liquid phase. The temperature employed in the thermal cracking step is preferably 390-500° C, more preferably 400-450° C, and the pressure is preferably atmospheric. It is preferred continuously to feed the plastics material to the thermal cracking step so that the level of the molten liquid phase in the cracking reactor is maintained substantially constant. The thermal cracking reaction is preferably carried out with stirring and in the presence of an inorganic porous particulate material. Whereas there is no particular limitation for the nature and size of the inorganic porous particulate material, provided that it is not deformed or deteriorated, it is usually preferably to employ porous particulate material having a size of about 1-10 mm. Illustrative embodiments of suitable porous particulate materials are natural zeolites, bauxite and red mud (residue remaining after removal of aluminum from bauxite). The porous particulate material may exhibit some cracking activity although this should be lower than that of the zeolite catalyst used in the subsequent catalytic conversion step.

Use of the inorganic particulate, material assists heat transfer during thermal cracking, inhibits attachment of coke to the reaction vessel, and lowers the boiling point of the vaporous product formed, thereby facilitating supply of the vaporous product to the catalytic conversion step and improving the quality and yield of the finally produced hydrocarbon oil. The amount of the inorganic particulate material is preferably at least 5% by weight, but can be up to 200-400% by weight, of the molten material in the reaction tank.

The paraffin-rich vaporous product formed in the thermal cracking step is then passed to a catalytic conversion unit containing a zeolite having a constraint index between 1 and 12. The term constraint index is defined in, for example, U. S. Patent No. 4,016,218. Examples of suitable zeolites include ZSM-5 (see U.S. 3702886), ZSM-11 (see U.S. 3709979), ZSM-12 (see U.S. 3832449), ZSM-23 (see U.S. 4076842), ZSM-35 (see U.S. 4016245) and ZSM-48 (see U.S. 4375573), although ZSM-5 is preferred. The zeolite is normally employed in its hydrogen form, although it may contain a metal such as platinum. The zeolite is also usually combined with a binder, such as alumina, and formed into particles having a size of 0.1-10 mm.

The catalytic conversion reaction is normally carried out at atmospheric pressure, WHSV of 0,8-0.85 and a temperature of 200-350° C, preferably of 250-340° C. The operation at such low temperature is unexpected and not only achieves economic advantages but also inhibits undesirable side reactions.

Use of the zeolite in the second cracking step not only allows a decrease in the cracking temperature and continuous operation but also improves the quality and yield of the product. Aging of the zeolite catalyst is found to be relatively slow and the present process can be conducted with a zeolite catalyst which has been regenerated after use in this or another reaction.

The resultant product is a hydrocarbon oil of low pour point demonstrating the occurrence not only of the cracking reaction but also of isomerization reactions. Absence of high molecular weight substances in the product is also evident. In fact, the hydrocarbon oil product contains only in substantial amounts of hydrocarbons having more than 22 carbon atoms. The hydrocarbon oil product can therefore be added directly to the gasoline blending pool. Gaseous by products are also obtained in the present process but these contain a substantial proportion of valuable C_3-C_5 compounds.

The invention will now be described below with reference to the accompanying drawing, which is a diagrammatic illustration of apparatus for performing a method according to one example of the invention.

Referring to the drawing the thermal cracking reactor is indicated generally at 1 and includes a feed supply zone 2, a thermal cracking reaction zone 3 and a stirrer 4 mounted on top of zone 3. The feed supply zone 2 supplies a screw feeder 5 which in turn feeds plastics material into the top of the thermal cracking reaction zone 3. Inside the thermal cracking reaction zone 3 are inserted a level meter 6 to measure height of the molten feed and a thermometer 7.

The top of the thermal cracking reactor 1 is connected to a catalytic reaction zone 8 which is filled with HZSM-5 having a particle size of about 3 mm into which is also inserted a thermometer 9. The bottom of the thermal cracking reactor 1 is provided with a gas burner 10.

The thermal cracking reaction zone 3 is maintained at the desired operating temperature by the burner 10, whereas the catalytic reaction zone 8 is maintained at its operating temperature by means of the heat capacity of the vaporous thermal cracking product, although an external heater (not shown) may also be employed.

The effluent from the catalytic reaction zone 8 is fed by way a cooling tube 12 equipped with a water-cooling condensor 11 to oil storage tanks 13 and 14 for collection.

In one practical embodiment, the apparatus shown in Figure 1 was constructed and operated as follows:

(A) The screw feeder 5 was of the two-axis screw type and was operated at a temperature of 330° C and a supply rate of 680-706g/hr.

(B)The thermal cracking reactor 1 was a cylindical tank 560 mm in height, 105 mm in diameter and 4.85 liter in volume. The thermal cracking reaction zone 3, namely, the molten liquid phase area of the reactor 1, was 250 mm in height, was filled with 250 g of natural zeolite produced in Kasaoka, Japan (particle size of approximately 0.5 mm) and was stirred at 8 rpm.

(C) The catalytic cracking reaction zone 8 was a cylindincal tower 300 mm in height, 76 mm in inner diameter and 1.36 liter in volume and was filled with 613 g of ZSM-5 in the hydrogen form.

The invention will now be more particularly described in the following Examples.

EXAMPLE 1

Polyethylene film, obtained as urban waste, was collected and pulverized to a size of approximately 5 mm. The pulverized feed was placed in the feed supply zone 2, heated to melting in the screw feeder 5 and fed to the first stage, thermal cracking reaction zone. The vaporous product thereby generated was passed to the second stage catalytic reaction zone 8 in which catalytic conversion was carried out. The conditions employed and the results obtained are summarized in the following table.:

Temperature in the first cracking stage (°C)	Temperature in the second stage catalytic conversion(°C)	Amount of feed (g/H)	Yield of Product (wt%)	Yield of hydro-carbon oil (wt%)	Specific weight	State of hydrocarbon oil product	Range of carbon numbers	Average molecular weight (Mn)	Proportion C_5-C_{14} components (wt%)
430 (1)	-	680	100	94.0	0.773	Wax at +20°C	C_5-C_{38}	197.3	39.6
430	270	680	45.3	83.9	0.742	liquid at -20°C	C_5-C_{18}	119.0	96.8
430	285	680	65.1	84.1	0.750	- do -	C_5-C_{18}	127.1	91.1
430	295	680	93.1	90.4	0.751	- do -	C_5-C_{20}	116.4	84.4
430	310	680	100	88.1	0.752	- do -	C_5-C_{19}	119.9	84.6
430	320	680	100	79.6	0.754	- do -	C_5-C_{19}	110.8	90.0
430	345	680	100	60.4	0.762	- do -	C_5-C_{14}	103.9	100
450 (2)	-	706	100	91.1	0.776	Wax at +20°C	C_5-C_{39}	210.0	36.2
450	257	706	34.0	77.4	0.742	liquid at-20°C	C_5-C_{17}	117.8	97.6
450	300	706	83.9	85.4	0.742	- do -	C_5-C_{19}	109.5	89.5
450	310	706	100	89.1	0.752	- do -	C_5-C_{21}	129.8	73.3
450	328	706	100	81.9	0.752	- do -	C_5-C_{20}	107.6	89.3
450	350	706	100	65.0	0.767	- do -	C_5-C_{15}	108.4	98.8

Note (1), (2) Comparative examples without the second stage cracking employed.

Analysis of a typical hydrocarbon oil product gave the following results:

Saturates 38.4%

Olefins 54.7%
Aromatics 4.5%
RON(clear) 62.5%

Analysis of a typical gaseous by-product of the process of gave the following results as a percentage basis of the entire gaseous component:
H_2 7.0: CH_4 8.0; C_2H_4 4.5; C_2H_6 7.6; C_3H_8 5.6; C_3H_6 19.9; i-C_4H_{10} 1.1; n-C_3H_{10} 9.8; i-C_4H_8 24.5; i-C_5H_{12} 0.5; n-C_5H_{12} 11.5.

Typical material balances were as follows:

	Wt% On Feed
Feed Polyethylene	100
Products	
- liquid	62
Gas	31
Carbon	7

EXAMPLE 2

The process of the preceding Example was repeated with two separate feeds, one consisting of particulate polyethylene and the other consisting of a particulate mixture of 90 wt% polyethylene and 10 wt% polystyrene. The results obtained are summarized as follows:

Feed	Polyethylene =100	Polyethylene/Polystylene =90/10
Properties of liquid product:-		
Sp. Gr.	0.7498	0.7878
Reid Vapor Pressure, kg/cm^2	0.78	0.45
RON	62.5	69.8
Distillation, °C		
Initial Boiling Point	30	38
5%	44	72
10%	60	89
20%	84	115
30%	108	136
40%	132	157
50%	159	182
60%	186	217
70%	216	257
80%	245	295
90%	279	334
95%	299	355
End Point	316	370
Residue (Vol %)	1.5	2.0

Claims

1. A process for preparing a normally liquid hydrocarbon product which comprises thermally cracking a plastics material in the molten liquid phase and catalytically converting the vaporous product thereby generated by contact with a zeolite having a constraint index in the range between 1 and 12.

2. The process according to Claim 1 wherein the vapor phase catalytic conversion is effected at a temperature in the range between 200 and 350° C.

3. The process according to Claim 1 or Claim 2 wherein the molten liquid phase thermal cracking is effected in the presence of an inorganic porous particulate material.

4. The process according to Claim 3 wherein the inorganic porous particulate material has catalytic cracking activity.

5. The process according to Claim 4 wherein the inorganic porous material is a naturally occurring zeolite.

6. The process according to any proceeding Claim wherein the liquid phase thermal cracking is effected

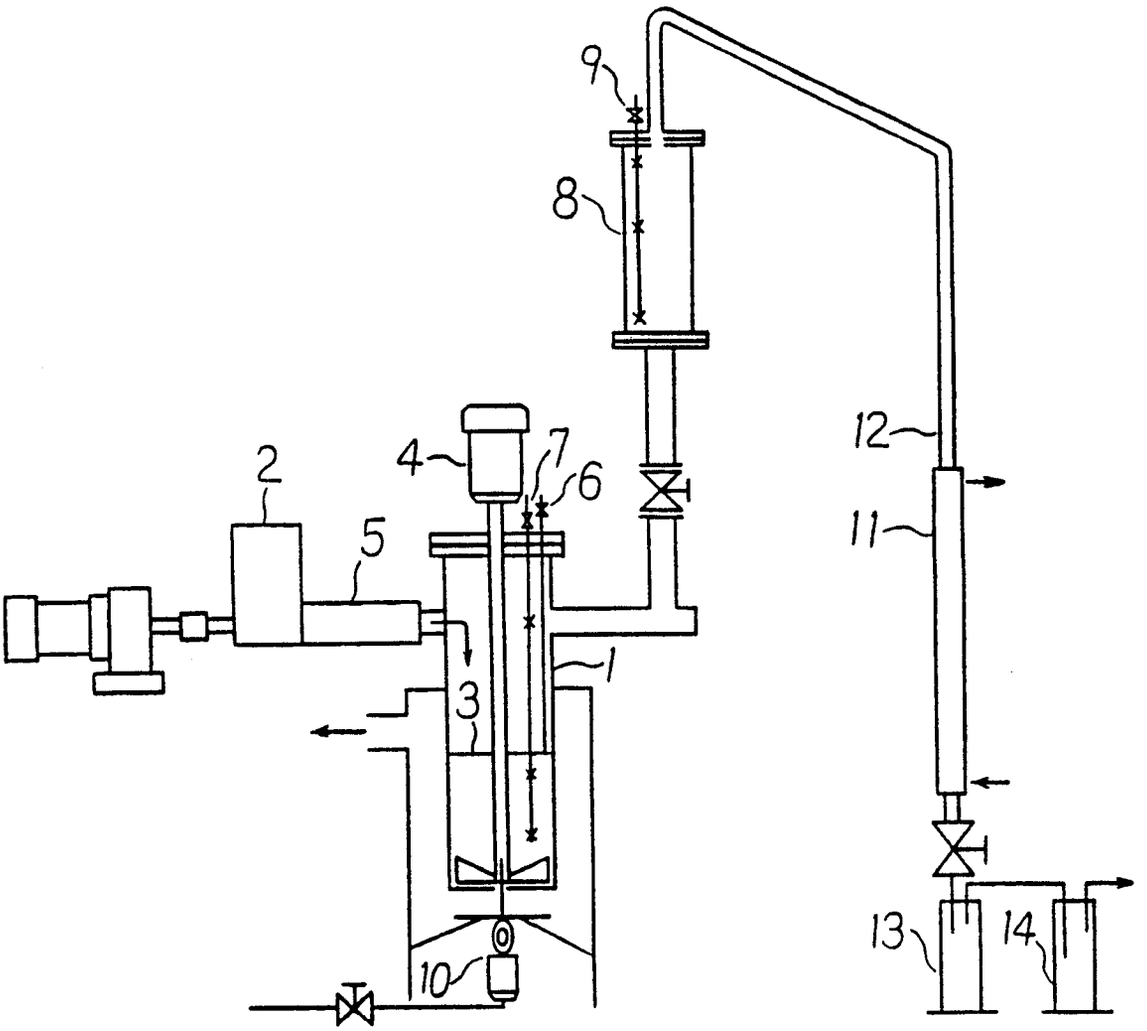
at a temperature in the range between 390 and 500° C.

7. The process according to any preceding Claim 1 wherein the zeolite used in the catalytic conversion step is ZSM-5.

8. The process according to any preceding claim wherein the plastics material is a polyolefinic plastic material.

9. The process according to Claim 8 wherein the polyolefinic plastics material is a homo- or copolymer of ethylene, propylene or butene.

10. The process according to any preceding Claim wherein the liquid product of the vapor phase catalytic conversion is substantially composed of hydrocarbons having carbon numbers not more than 22.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