(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
25 January 2001 (25.01.2001)

PCT

(10) International Publication Number
WO 01/05908 A1

(51) International Patent Classification[7]: C10G 1/10

(21) International Application Number: PCT/CN00/00196

(22) International Filing Date: 13 July 2000 (13.07.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
99 2 16787.6 16 July 1999 (16.07.1999) CN

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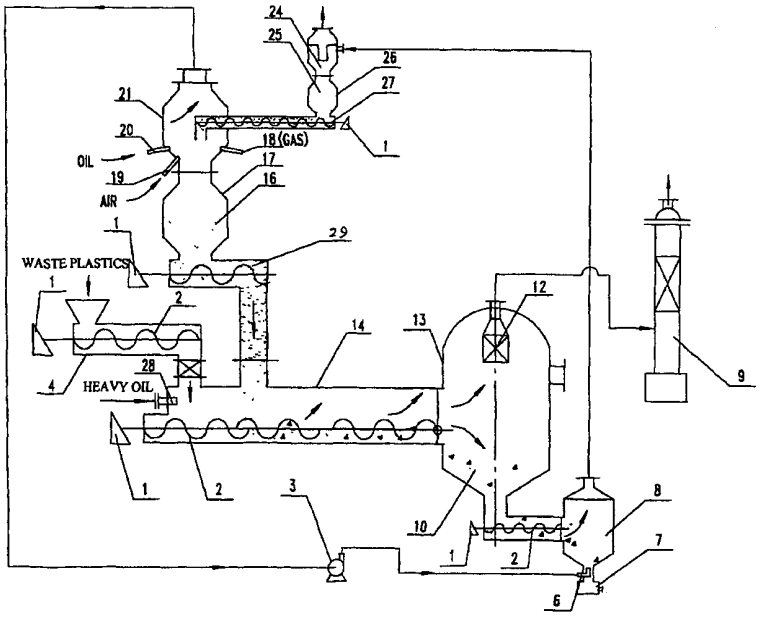
(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

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.

(54) Title: A PROCESS FOR PRODUCING GASOLINE AND DIESEL FROM WASTE PLASTICS AND/OR HEAVY OIL



(57) Abstract: The invention relates to a process for producing gasoline and diesel from waste plastics and/or heavy oil and comprises the steps of: (a) mixing waste plastics and/or heavy oil with a first catalyst in a pyrolysis reactor at a high temperature to carry out a pyrolysis and a first catalytic cracking; and (b) introducing the products in step (a) into a fixed bed to perform a second catalytic cracking with a second catalyst. The process further comprises the step (c) recycling the first catalyst in the reaction.

WO 01/05908 A1

A PROCESS FOR PRODUCING GASOLINE AND DIESEL FROM WASTE PLASTICS AND/OR HEAVY OIL

Field of the Invention

The present invention relates to a process for producing low-boiling point hydrocarbons from waste plastics and/or heavy oil, and more particularly to a process for producing gasoline and diesel through pyrolysis and catalytic cracking of waste plastics and/or heavy oil.

Background of the Invention

Many methods for preparing low-boiling hydrocarbons from waste plastics and high-boiling hydrocarbons are known. U.S. Patent No. 4,851,601 and EP-A-0607862 (Applicant: MAZDA MOTOR CORPORATION) disclose a reaction of pyrolysis in a reactor kettle (vertical or horizontal), wherein the outside wall of the kettle is heated at a high temperature while the materials therein are heated indirectly.

In this method, the outside wall is apt to be deformed when the reactor is heated directly at a high temperature. The materials are readily sintered on the inside wall because of local over-heating so that the conversion yield of the reaction and the life of the reactor are greatly decreased. In addition, the coefficient of the reactor's heat transfer is relatively low, it is difficult to drain the reaction residues, and the

catalytic reaction in the fixed bed needs a separate heat supply. These are the common drawbacks of the reactor kettle in the prior art.

A spiral reactor utilized in some special fields is similar to the above. Heat is indirectly transferred when it works. The outside wall of the reactor is heated directly at a very high temperature, making the materials in the reactor indirectly heated. Therefore, the heat transfer coefficient is not satisfactory. Particularly, because the screw therein is apt to be deformed at a high temperature, making it hard to seal the two ends of the screw so that gas generated in the reaction may be exhausted.

Summary of the Invention

Accordingly, an object of the invention is to provide a process for producing gasoline and diesel from waste plastics and/or heavy oil (including high-boiling hydrocarbons) to overcome the shortcomings in the prior art as described above.

The process of the present invention comprises the steps of:

(a) mixing waste plastics and/or heavy oil with a first catalyst at a high temperature in a pyrolysis reactor to carry out a reaction of pyrolysis and first catalytic cracking simultaneously; and

(b) introducing the products in step (a) into a fixed bed to perform a reaction of second catalytic cracking.

Said first catalyst is made as follows: powder Al_2O_3 is mixed with water glass to obtain a slurry, and the resultant slurry is then mixed with catalyst HZSM-5. The resultant mixture is dried, formed, granulated, and heated to obtain the first catalyst.

The ratio between powder Al_2O_3 and water glass is 1:3-5 by weight and that between the slurry and HZSM-5 is 1:0.2-0.5 by weight.

According to the process of the invention, the materials can be converted to gasoline and diesel with a high yield, and the requirements for the reactor are not strictly defined because the first catalyst is used to heat the materials directly.

Brief Description of the Drawing

Figure 1 is an operational flow chart of the process in the invention.

Detailed Description of the Invention

The process of the present invention comprises the steps of:

(a) mixing waste plastics and/or heavy oil with a first catalyst at a high temperature in a pyrolysis reactor to carry out a reaction of pyrolysis and first catalytic cracking simultaneously; and

(b) introducing the products in step (a) into a fixed bed to perform a reaction of second catalytic cracking.

The process of the invention further comprises a step of:

(c) recycling the first catalyst in the reaction.

The reaction of pyrolysis and first catalytic cracking may be conducted under the standard atmosphere or higher, and the temperature of the first catalyst may be controlled at 500-1,000°C, preferably 600-700°C.

The reaction of second catalytic cracking is carried out with a second catalyst in the fixed bed at 300-600°C, preferably 300-450°C.

The second catalyst used in the invention may be the commonly used catalyst in the reaction of catalytic cracking in the art.

In the invention, the first catalyst after being heated to a high temperature in the combustion chamber the first catalyst is charged into a pyrolysis reactor by using a spiral conveyor. Waste plastics (or heavy oil) are charged into the sealed pyrolysis reactor, and there they are directly mixed with the hot first catalyst to perform a reaction of pyrolysis and first catalytic cracking. The materials are decomposed into gaseous hydrocarbons and residues. The gaseous hydrocarbons then enter a fixed bed in the reactor and are further decomposed into smaller molecules via a second catalytic cracking. Gaseous substances from the reaction are collected by means of the conventional process in the prior art so as to obtain gasoline and diesel. Said first catalyst and residues in the reaction are introduced into a gasification chamber by a screw, and further into a separator by a spiral conveyor. Hot flue gas is led into the separator

with a blower, which blows said mixture into a cyclone separator so as to collect a solid mixture. Said mixture is introduced into a combustion chamber by a spiral conveyor. In the combustion chamber, organic substances in the mixture are burnt out, while the first catalyst is heated and delivered to the spiral reactor again.

In the above-mentioned process, the feedstock is mixed directly with hot first catalyst, and pyrolysis and the first catalytic cracking take place at the same time. The first catalyst is not only used as a heating medium but also as a catalyst, which can be recycled.

Said first catalyst is made as follows: powder Al_2O_3 is mixed with water glass to obtain a slurry, and the resultant slurry is then mixed with catalyst HZSM-5; and the resultant mixture is dried, formed, granulated, and heated at a temperature of 550-800°C. The ratio between powder Al_2O_3 and water glass to be used is 1:3-5 by weight and that between the slurry and HZSM-5 is 1:0.2-0.5 by weight. Said first catalyst used in the invention is generally of a Mohs' scale of hardness of 7-9 and a diameter of 0.2-0.5mm.

In the above process, said pyrolysis and first catalytic cracking may be conducted under standard atmosphere or higher. The reaction temperature, when the first catalyst is transmitted from the combustion chamber to the pyrolysis reactor, is controlled at 500-1000C, preferably 600-700°C. The temperature of the first catalyst is kept at 400-800°C,

preferably 500-600°C when it leaves the pyrolysis reactor.

Said second catalytic cracking is carried out in the fixed bed inside the gasification chamber. Heat required in the second catalytic cracking is provided by the gasification chamber itself. The second catalytic reaction is undertaken at 230-600°C, preferably 300-450°C. A particular catalyst DL-1 being composed of (Wt. %): 8% of CHO-1(a commodity produced by China Qilu Petrochemical Factory), 24% of REY, 25% of flokite (silicon/aluminum =12/1) and 43% of catalyst ZSM-5 is used in the second catalytic cracking after being thoroughly mixed and calcined.

The present invention will be more distinct with reference to the accompanying drawings.

Referring to Fig. 1, a first catalyst 16 in the granular form is charged into a combustion chamber 21 from a storage tank 26 with a spiral conveyor 27. Fuel oil (or recuperated pyrolysis gas) and air are sprayed into the combustion chamber 21 simultaneously via nozzles 18, 19 and 20. The first catalyst 16 in the combustion chamber 21 is heated to 500-1,000°C and subsequently led into a storage tank 17. A spiral conveyor 29 is started by a motor 1 to push the first catalyst 16 continuously into a pyrolysis reactor 14. At the same time, the materials to be treated are pushed by a screw (or reciprocating) extruder 4 into a spiral reactor 14. If the materials are heavy oils, they may be pumped into the sealed

pyrolysis reactor 14 via an inlet 28. The materials are mixed directly with the first catalyst 16 in the reactor 14 to undergo a pyrolytic reaction and a first catalytic cracking. Rotated and pushed by the spiral conveyor 2, gaseous hydrocarbons generated from the reaction and residues move forward to enter a vaporizer 13. Gaseous hydrocarbons enter a fixed bed 12 in the vaporizer 13 through the vaporization region, and react with a second catalyst to generate gaseous hydrocarbons with small molecules, which will be fractionated in a fractional column 9 to obtain gasoline and diesel by means of the conventional process. A mixture 10 of reaction residues and the first catalyst 16 entering the bottom of the vaporizer 13 is driven into a separator 8 via a spiral conveyor 2. A blower 3 is employed to push the high-temperature flue gas into the separator 8 via an entrance 6. Solid mixture 25 containing the first catalyst are flown up to enter a cyclone 24 because they are lighter. Other heavy residues enter the bottom of the separator 8 and are discharged from a hole 7. Thus, the solid mixture 25 in the cyclone 24 drops into a storage tank 26, and then is charged into the combustion chamber 21 by the spiral conveyor 27. In the combustion chamber 21, organic substances in the mixture 25 are burnt out and inorganic dusts are extracted together with high-temperature flue gas. The first catalyst 16 is hereby recovered and falls into the storage tank 17, subsequently. The heated first catalyst is then charged into the reactor 14 by the spiral conveyor 29.

The invention is further described by the following examples.

Example 1

Water glass (1,600kg, modulus>3) and powder Al_2O_3 (400kg) were completely mixed to obtain a slurry. The slurry was mixed with catalyst HZSM-5 (800kg). The resultant mixture was dried, formed, granulated, and heated at 800°C for 4 hours to obtain the first catalyst with a Mohs' scale of hardness of 8.5 and a diameter of 0.4 mm.

2,000 kg of the first catalyst prepared as indicated above was charged into the combustion chamber 21, and simultaneously sprays $0^{\#}$ diesel (or recuperated pyrolysis gas) and air were led into the combustion chamber 21 to burn. The first catalyst was heated up to 600-700°C and then led into the pyrolysis reactor 14. The screw (or reciprocating) extruder 4 was used to push 1,400kg of waste plastics (PP25%, PS25%, and PE50%) into the reactor 14 to perform the reaction. The temperature at the stock inlet of the reactor 14 was controlled at 600-700°C, whereas the temperature at the residue outlet thereof was controlled at 500-600°C. The catalyst DL-1 was arranged in the fixed bed 12, and the second catalytic reaction was conducted therein. The reaction pressure was kept at 0.05-0.1 MPa. Gasoline and diesel were obtained from the fractional column 9. The mixture of the first catalyst and residues was charged into the combustion

chamber 21 and was heated up to 600-700°C therein to separate the first catalyst. The recovered first catalyst was introduced into the reactor 14 for heat supply.

Products generated from this Example are listed below:

1. Gasoline, 630kg, RON=93.5, components (by wt%): paraffin 19.9%, cyclanes 12%, olefin 48%, arenes 9.9%, others 10.2%;
2. Diesel, 420kg, cetane value=52, components (by wt%): paraffin 15%, cyclanes 8%, olefin 55%, arenes 10%, others 12%;
3. Inorganic residues 140kg;
4. Flammable gas 210kg.

What I claim is:

1. A process for producing gasoline and diesel from waste plastic and/or heavy oil comprises the steps of:

(a) mixing waste plastic and/or heavy oil with a first catalyst in a pyrolysis reactor at high temperature to carry out a pyrolytic reaction and a first catalytic cracking ; and

(b) introducing the products in step (a) into a fixed bed to perform a second catalytic cracking with a second catalyst.

2. A process as claimed in Claim 1, wherein said first catalyst is made as follows: powder Al_2O_3 is mixed with water glass to obtain a slurry, and the resultant slurry is then mixed with catalyst HZSM-5; and resultant mixture is dried, formed, granulized, and heated at 550-800°C.

3. A process as claimed in Claim 2, wherein the ratio between powder Al_2O_3 and water glass is 1:3-5 by weight and that between the slurry and HZSM-5 is 1:0.2-0.5 by weight.

4. A process as claimed in Claim 3, wherein said first catalyst is of a Mohs' scale of hardness of 7-9, and a diameter of 0.2-0.5mm.

5. A process as claimed in Claim 1, wherein the process further comprises the step of:

c) recycling the first catalyst in the reaction.

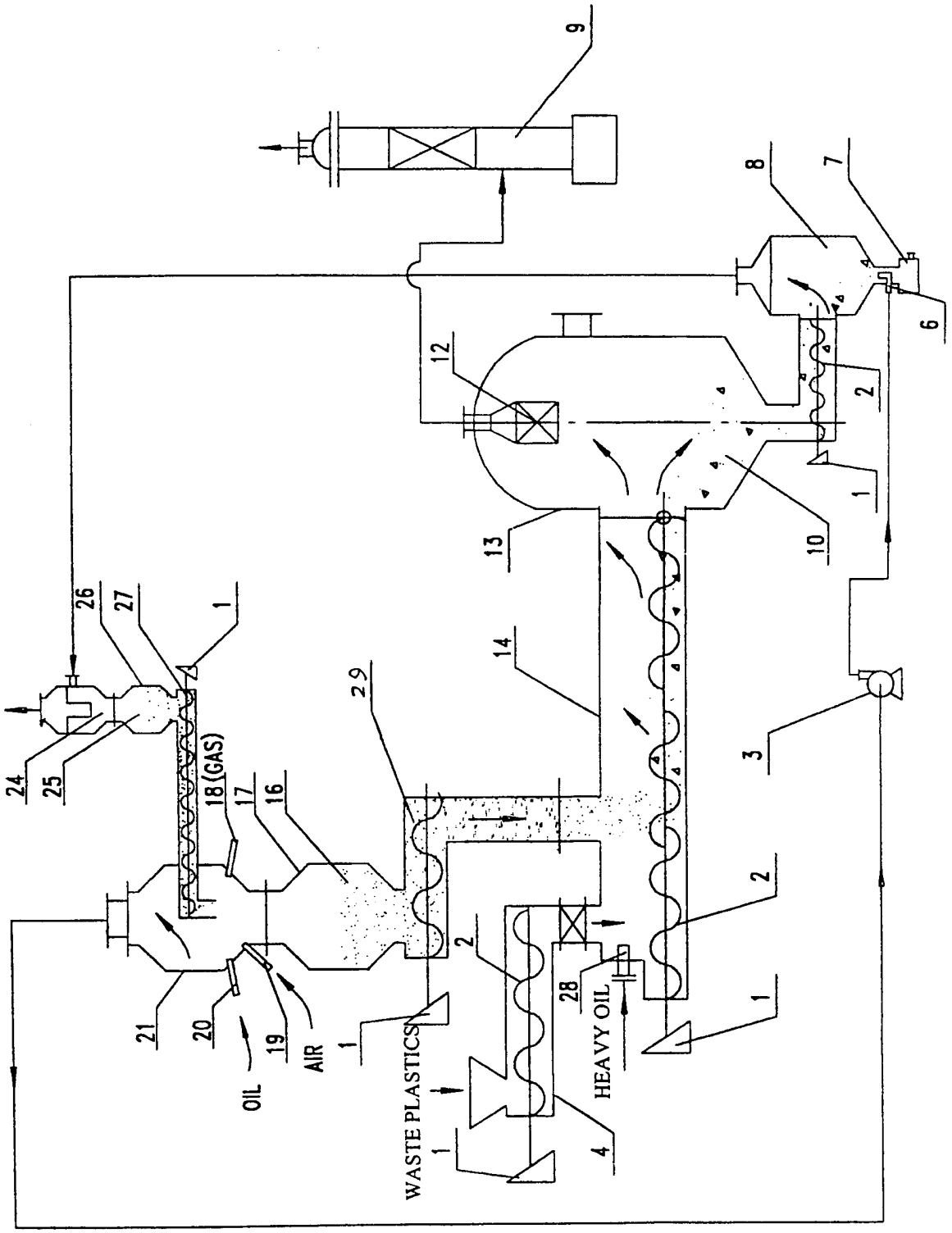
6. A process as claimed in Claim 1, wherein said catalyst in the fixed bed

comprises 8% of CHO-1, 24% of REY, 25% of flokite and 43% of catalyst ZSM-5, by weight.

7. A process as claimed in Claim 1, wherein the process is performed under the standard atmosphere or higher.

8. A process as claimed in Claim 1, wherein the temperature of the first catalyst is controlled at 500-1,000°C before entering the pyrolysis reactor, and is controlled at 400-800°C while leaving the pyrolysis reactor.

9. A process as claimed in Claim 1, wherein the first catalyst advances in the same flow direction as that of the waste plastics and/or heavy oil.


9
8
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12
2
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10
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14
29
3
26
27
1
24
25
18 (GAS)
17
16
2
2
28
HEAVY OIL
1
21
20
19
OIL
AIR
1
WASTE PLASTICS
1
4

FIG. 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN00/00196

A. CLASSIFICATION OF SUBJECT MATTER

IPC[7] C10G1/10

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)

IPC[7] C10G1, C08J11

Documentation searched other than minimum documentation to the extent that such documents are included in the field searched

Electronic data base consulted during the international search(name of data base and, where practicable, search terms used)

WPI, CNPAT

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant claim No.
A	CN1232861A(Xing Li) 27. Oct. 1999 claims; Figures	1-9
A	CN1075328A(Zhao Taiping)18. Aug. 1993 claims	1
A	EP607862 A1(Mazda Motor Corporation)27. Jul. 1994 claims; figure1	1

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"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 being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
16 September 1999 (16. 09. 99)	16 NOV 2000 (16.11.00)
Name and mailing address of the ISA/ China State Intellectual Property Office 6, Xitucheng Road, Jimen Bridge, Haidian District, Beijing, 100088, P. R. China Facsimile No. 86-010-62019451	Authorized officer Lei Chunhai Lei Chunhai Telephone No. 86-010-62093933

Form PCT/ISA/210(second sheet)(July 1992)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN00/00196

Patent document cited in search report	Publication date	Patent family members	Publication date
EP607862	27.Jul.1994(27.07.94)	JP6220461	9.Aug.1994(09.08.94)