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CA 2571264 C 2013/01/08

(11)(21) **2 571 264**

(12) **BREVET CANADIEN
CANADIAN PATENT**

(13) **C**

(22) Date de dépôt/Filing Date: 2006/12/14

(41) Mise à la disp. pub./Open to Public Insp.: 2008/04/10

(45) Date de délivrance/Issue Date: 2013/01/08

(30) Priorité/Priority: 2006/10/10 (UY29851)

(51) Cl.Int./Int.Cl. *C10G 1/02* (2006.01),
C10G 7/00 (2006.01)

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(54) Titre : UN PROCEDE POUR OBTENIR DE L'HYDROCARBURE LIQUIDE AU MOYEN DU CLIVAGE DE
MOLECULES DE CARBONE ET D'HYDROGENE

(54) Title: A PROCESS TO OBTAIN LIQUID HYDROCARBONS BY CLEAVAGE OF CARBON AND HYDROGEN
MOLECULES

(57) **Abrégé/Abstract:**

Process to obtain liquid hydrocarbons by cleavage of carbon and hydrogen molecules using materials with chemical waste, textile waste, biomass and whatever kind, being the same milled by a turbine and transferred to the main chamber, increasing its temperatures to eliminate water, there is application of kinetic energy and friction with selected reactants to cleave the chains and separate the above mentioned elements and restructure the long or short chains to obtain the selected hydrocarbons by distillation and condensation.



ABSTRACT

5 Process to obtain liquid hydrocarbons by cleavage of carbon and
hydrogen molecules using materials with chemical waste, textile waste,
biomass and whatever kind, being the same milled by a turbine and transferred
to the main chamber, increasing its temperatures to eliminate water, there is
application of kinetic energy and friction with selected reactants to cleave the
10 chains and separate the above mentioned elements and restructure the long or
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condensation.

A PROCESS TO OBTAIN LIQUID HYDROCARBONS BY CLEAVAGE OF CARBON AND HYDROGEN MOLECULES

The present invention studies the solution of a serious universal problem, namely, the real lack of fuels to satisfy the high demand of these days, added to the continuous search of fuels that do not derive from petroleum and the effort to decrease environment contamination.

I. Background of the Invention

There are several ways to obtain fuels. For instance, a refinery is a large complex in which crude oil undergoes distillation or physical separation and later chemical processes. Petroleum may be classified in four categories: Paraffinic, naphtenic, asphaltic or mixed based crude and aromatic crude.

Refineries differ a lot between each other, depending on the technologies and process diagrams used, as well as on their capacity. The purpose of such may be to process soft crudes, heavy crudes or mixed based crudes. Refinery is carried out in several stages. The first step of the refinery process of crude oil is completed in the "primary distillation" towers. Within these towers, the same function nearly at atmospheric pressure and they are divided in many sections. The crude reaches these towers after passing by an oven, in which it is "baked" and turned into steam. This steam enters through the lower part of the distillation tower and elevates between the trays. As it elevates, it loses heat and cool. When each steamed component finds its own temperature, it condensates and deposits in its corresponding tray, which connect with certain ducts for the recollection of the different currents split in this stage. The "reduced crude" falls in the bottom of the tower, that is, the crude which did not evaporate in this first stage. Therefore, the "vacuum distillation" tower receives the reduced crude of the first stage and removes heavy gasoil, paraffinic bases and residues. The Cracking unit receives reduced gasoil and crudes to produce main gasoline and propane gas. The basic refining tool is the distillation unit. Hydrocarbons with lower molecular mass evaporate at lower temperatures, and larger molecules evaporate as the temperature rises. The first material

distillated from crude is the gasoline fraction, followed by naphtha and finally kerosene. On the other hand there is the thermal cracking process, developed in an effort to increase the yield of distillation. In this process, the heavier parts of the crude are heated at high temperatures under pressure. Said process
5 cracks the larger hydrocarbon molecules into smaller molecules, which in turn increases the amount of gasoline – composed of these molecules - obtained from a barrel of crude.

Later, a carbonization process in which fluids recirculate was invented;
10 The process demanded a longer time and resulted in a much lower accumulation of coke. Many refiners adopted this pressurized pyrolysis process.

In the 1930s other two basic processes were introduced; alkylation and catalytic cracking, which additionally increased the gasoline produced from a
15 crude barrel. Manufacturing these products has given origin to the gigantic petrochemical industry, which produces alcohols, detergents, synthetic rubber, glycerin, fertilizers, sulfur, solvents and raw materials to produce medication, nylon, plastics, paintings, polyesters, additives and food supplements, explosives, dyes and insulating materials.

20

The exhaustion of cheap crude and the imminent fuel crisis have determined the implementation of alternative crudes such as bio diesel and bio ethanol which “are neutral in the production of carbon emissions”. When bio fuels are burned the carbon dioxide absorbed by plants as they grew in the field
25 is returned to the atmosphere. The impairment of these alternatives is simply that there is not enough land that may be ploughed to cultivate all the bio fuel necessary to satisfy the voracious appetite for this source of energy of industrialized countries. Bio diesel has also given a solution to the superabundance of genetically modified crops (transgenic) which are today
30 being turned down by consumers all over the world. According to the bio diesel industry, to process bio fuels it is necessary to build large refinery plants close to agricultural areas or forests, where raw material is abundant. Thus, bio diesel must be transported to the service stations just as crude is.

On the other hand, methanol is an alternative fuel to avoid the toxicity of naphtha emissions and destruction of the ozone layer. Likewise, the caloric power of naphtha is approximately twice as high as the caloric power of methanol, therefore it is more profitable. Originally, methanol was produced by destructive distillation of wood chips. This raw material was named wood alcohol. This reaction uses high pressure and temperature, and requires large and complex industrial reactors. There are different processes to obtain methanol such as: Lurgi process and ICI process.

Upon development and analysis of the processes already known, and with the purpose of introducing the object of the invention of the present application, we should explain some of the advantages of the invention proposed which overcome in great extent the different distillation processes of crude, reduce pollution and harness natural resources.

In our novel process natural raw materials are used, such as biomass, wastes of whatever nature (explained herein below) in which the caloric power of raw materials guarantee its transformation into gasoil or other hydrocarbons, the volume of which shall be equal to 80% of its caloric power.

That is, 1 kg of gasoil of 8000 kcal is produced with four kilograms of raw material of 2500 kcal/kg.

A further object of the invention is to be able to convert through this process the initial raw material, hard to value, into a fuel of easy valuation and application. A further advantage is its variety of mechanical applications, which improves its performance. For example, if biomass is used to produce electricity with the steam turbine boiler cycle we would have a performance of 22%. But if we convert this same biomass into gasoil with a performance over 80%, and this gasoil is used in an electrical central unit of combined cycle with a performance of 55%, the total performance would be 44%.

Today, the fuel of the invention may be used in transportation, but not the raw material. In this process, two liters of gasoil shall be produced for each kilowatt consumed. In some cases the gasoil produced in the process may be

slightly muddy, which may be due to the raw material used or to an alteration of the process. For this reason, a distillation tower shall be provided, separated from the main process, in which a second distillation shall be performed, where the residues of this process are returned to the main chamber. The water recollected in the condenser passes by a filter system to settle hydrocarbons dragged by said water. Said hydrocarbons are returned to the main chamber. Later, said water is distilled and does not bring any complications associated thereto. In relation to the solids recollected at the end of the main process, if the facility is large enough, there is a possibility to recollect part of the zeolites (if this material is used) which have been precipitated or dragged by inorganic substances. There is raw material such as lignin of the wood which contains a significant higher amount of carbon atoms than hydrogen molecules, which produces a great amount of coke carbon. Coke carbon is later recovered, by separating it from the rest of the solid residues by elutriation. If raw material is rice straw and husk, the silicon contained therein would be recovered. In case of paper slurry silicon, alumina and carbon is recovered. From high sulfured crude, which is useless for conventional distillation, high amounts of sulfur may be obtained. Many other examples could be mentioned. Components may be separated from each other by several technologies, and the most suitable shall be applied for each particular case. One liter of gasoil in a small plant may amount to USD 0.21, whilst in a large plant amounts to USD 0.16. Raw material is found in any country, nature offers plenty chemical reactants; facilities may be built in all countries because the only requirement is stainless steel boilers, and turbines, on the other hand, control instruments and vacuum pumps are very common and they are highly available in the market.

25 The process does not increase CO₂ production, and for biomass there is negative production of CO₂, therefore there is compliance with the Kyoto treatment in this respect. With this technology it shall be possible to eliminate dumps, which are the main pollution spots for underground waters and for methane discharge into the atmosphere.

30 In one aspect, the present invention provides a process to obtain liquid hydrocarbons from the breaking of carbon and hydrogen molecules of a hydrocarbon not derived from petroleum that comprises a first physical/mechanical stage and a second chemical stage, characterized because in the physical/mechanical stage trituration, shearing and friction of the hydrocarbon

not derived from petroleum with reagents that produce exothermal reactions, where said reagents comprise zeolyte pearls, to rise the temperature and break the molecules are produced and in the chemical stage because they use reagents that comprise zeolytes based on sodium or calcium to neutralize the
5 reactions not desired within the process and to guide said process to the production of liquid hydrocarbons.

II. Detailed description of the Invention

The object of the present invention is to obtain liquid hydrocarbons by cleavage of carbon and hydrogen molecules as components of biomass, urban solid residues, recycled materials, vehicle, hospital residues as well as petrochemical, textile residues, meat residues, animal fat, leather and excrements among others.

The industrial facilities in which the process of the present invention is carried out shall be named SMRF and said process shall be a physical-chemical process. Starting by a physical-mechanical process, in which there is milling, shearing, and friction of the raw material with dusted exothermic material, the most frequent of which are synthetic zeolite beads such as those used in petrochemical industry. This first process causes the section of raw material to reduce its size up to molecular dimensions and further breakage of the molecular bonds with friction. The second process is a chemical process, in which reactants shall be used, such as zeolites (composed of sodium and calcium bases) as well as sodium, calcium, potassium or magnesium commonly used (depending on the raw material used) to neutralize the unwanted reactions and to lead the process to obtain the desired liquid hydrocarbons.

To start the process of this invention the raw material should be modified, so if the same contains suspended water, temperature shall be increased to 240°C by heat exchangers; in said first stage it shall be completely dehydrated. Later on, it shall be introduced into the main process at the same temperature, while the dehydrated raw material may be incorporated directly to the process. Viscous humid material shall be treated as already described herein. While highly viscous dehydrated materials may also be treated at temperatures below 240°C to decrease viscosity and increase fluidity which improves the inclusion of the same in the main system (i.e: tar). Solid dehydrated material (i.e: plastics) shall receive a previous milling process up to 3 mm, which is small enough to be introduced directly in the process herein. Solid humid raw material (i.e: biomass) shall receive a previous milling treatment up to a 3 mm section simultaneously with the drying process. Said standard drying process in the market (accomplished by several procedures) shall yield raw material with 10% and 15% of humidity since a 10% reduction is very difficult for biomass. It

is then normally introduced to the process. It shall also be necessary to carry out the previous treatment of said material which contains crystalline water, which cannot be eliminated in the first state of the process.

5 MAIN PROCESS

In this stage of the process of the present invention there is analysis, acknowledging and quantification of the chemically active substances at temperatures under 400°C, as well as inorganic molecules linked to the chains
10 of molecular carbon and hydrogen. The recurrent elements are halogen, chloride and fluoride, which are in turn treated with lime, sodium, potassium or magnesium; those hardly ever found are mercury and chrome, heavy metals, active at process temperatures, but they are neutralized by ions (which shall react with other ionic substances). The process demands the presence of an
15 essential element. Its main properties are: state (fine powder), shape (must allow an easy friction with the raw material molecules) and it must be exothermic. These materials are commonly used in chemical industries and they can be soil or clay, containing aluminum and silicon, aluminum chlorides, but most used are synthetic zeolites which are highly available, since they have
20 been used in petrochemical industry since the 60s. These materials make it possible to control temperatures during the process, since the main function is to produce friction with raw material molecules by friction within the turbine. The exothermic feature produces the temperature of materials to rise. Therefore, to initiate the feed of raw material it must be mixed with reactants and Zeolite; the amounts
25 shall depend on the previous analysis.

Once the raw material is prepared in the conditioning process to start with the main process, there follows the description of the "Main Process".

30 Initially, the main chamber and the turbine circuit shall be filled up with oil produced by liquid saturated hydrocarbons, then the turbines are turned on until the temperature reaches approximately 370°C which means the plant is in shape to receive raw material selected with reactants, usually zeolites or other exothermic reactants. The volume of raw material introduced in the main

chamber is limited to its capacity and to the fluid viscosity, since when raw material is added the fluid viscosity increases and the process works until fluid viscosity is such to allow flows in the oil. Most of turbines with double chamber are self-priming pumps, otherwise, it will be needed a force feed pump to send the flow
5 towards the turbine. This flow is composed of oil and raw material, which is strongly sheared when entering the turbine, causing a decrease of dimension up to the size of colloids (about 20 micron), and friction among molecules of raw material with zeolite (or others), added to the mechanical action of the turbine produces heat, the fluid temperature increases up to 270 to 400°C during the process,
10 depending on the raw material used. Raw material reduced to colloid dimensions (nearly molecular) guarantees reaction of active chemical substances within them, both free and bonded to its hydrogen and carbon molecules. Said active chemical substances shall be neutralized by the reactants provided. Oxygen atoms shall be free and may be bond to a carbon within free CO₂, which causes
15 cleavage of initial chains of carbons. If said chains are short, vaporization temperatures shall be under or equal to the temperatures of the process, and this may produce linkage of said chains; on the contrary, if chains are long, their vaporization temperatures shall be higher than the temperature of the process therefore there is saturation of the molecule and loss of one or more carbon
20 atoms. Crystalline water molecules within the raw material shall be free by shearing and friction. Likewise, any kind of water molecule in humid shape shall evaporate.

25 Any molecule formed by carbon and hydrogen atoms, however saturated and chemically stable shall be under kinetic strength and friction with zeolites (or any other element) within a turbine; therefore the same shall break in a process resembling petrol cracking. This is the more significant effect of the process of these presents.

30

The process temperature shall not be constantly over 400°C, since temperatures over 400°C may produce mechanical damage to the turbine, therefore it is necessary to refrigerate the turbine. Temperatures should not be

over 400°C from the chemical point of view either to avoid occurrence of the carbonization process as well as tar formation.

At the outlet of the turbine light hydrocarbons exits as vapor and higher hydrocarbons exit as liquids (oils). Those hydrocarbons that exit as vapor are absorbed by the negative pressure of the distillation tower, whilst those liquid hydrocarbons precipitate in the main chamber depending on its density in relation to the downward flow. The heavier oils are the first to enter in the turbine cycle. The inorganic solid materials and those coming from the chemical reactions precipitate in the bottom of the main chamber. In the distillation tower, hydrocarbon vapors flow from inside of condensed oils in its different sections, which have the density provided by the distillation tower, these vapors exit through the upper section. Heavier molecules return to the main chamber to undergo once more the process (this is essentially the normal process of a distillation tower).

Water and oil vapor molecules overcome the process of the distillation tower and exit as vapor by the upper part, and then they pass by a heat exchanger the flow of which is fed by the vacuum pump at the outlet of the same, inside, vapours condensate and pass by a separator in which mater coming from hydrocarbons is separated from them. These hydrocarbons represents the end of the process: automotive gasoil.

There exists a gas purger for the outlet of CO₂ derived from raw material molecular oxygen, generally the amount of the emission is very low, the emission shall be high for glycerin and alcohols. Solid residues remaining at the end of the process precipitate in the bottom of the chute shaped main chamber and they are extracted through a tube and an on-line valve which opens when the same reach certain level of the chute. These solid remains are impregnated with liquid hydrocarbons, therefore they are transferred through a heat exchanger or electric resistance to evaporate these hydrocarbons and they are returned to the upper part of the main chamber. These solids generally include: Inorganic remains carrying raw material, products of the chemical reactions and remains of zeolites reactants (or others).

In short, in the process of the present invention there is complete restructuring of raw material molecules to obtain the desired saturated hydrocarbon vapors. The main effect of the process is the high shearing
5 produced by the turbine and the friction therein with the exothermic material. These two actions together cause breakage of physical and chemical structures of raw material into its components. Inorganic components form solids and CH_2 components form saturated liquid and gas hydrocarbons, water vaporizes and oxygen atoms associate with carbon atoms forming CO_2 . Carbon atoms which
10 have not bonded with available hydrogen atoms form bonds between them. This event produces coke carbon granules. Without reactants and its neutralizing effect the desired effect would not be produced, because in the event of active chemical substances, said substances would be part of the process and other substances than the desired substances would be produced.

15

The process temperature is the required one, which is not higher than the vaporization temperature of desired hydrocarbons. The function of the main chamber is to separate substances by their density.

20 Molecules containing oxygen atoms, as described before, lose the oxygen atom and the carbon atoms forming CO_2 , in long chains this implies their cleavage, while in short molecules such as alcohols, glycerin, etc, the effect is the opposite and molecules link into a larger chain. To obtain polymers from alcohols the process is the same, but it is achieved at lower temperatures
25 when polymers are obtained from zeolites.

30

IV. Procedure to carry out the invention.

FLOWS OF MAIN PROCESS

5 There is only one entrance. If there is more than one turbine the entrance is subdivided into one per turbine. Through this entrance the following enter: Selected raw material and the pulverized chemical reactants required.

10 There are four exits, three of which are located at the exit of the condenser, one of them for the selected hydrocarbon (gasoil), the second one for water and the third one for gases. The fourth exit is located at the bottom of the main chamber for solid residues.

HOW IS THE PROCESS CONTROLLED?

15

- Inlet of raw material into the process

The volume of raw material depends on two parameters: the oil level in the cycle since the process is limited to a predetermined capacity. The second factor is the material viscosity found in the turbine- main chamber circuit since material should be fluid enough to allow it proper circulation, since income of high amounts of solid material or very viscous material could increase its viscosity, which would produce a fluid with unsuitable circulating properties and thus there would be disturbance of turbine operation.

25

- Process Temperature

The process should be carried out at constant temperature with a temperature range such that selected hydrocarbons are evaporated. To achieve this temperature, and to further maintain or regulate this temperature value, there should be a suitable relation between exothermic material and zeolites (or others) depending on the temperature of the process.

30

- Fluid pH

pH is the indicator of the proportion of reactants needed, since distortion of the pH scale (higher or lower) indicates which is the reactant that should be added and in what proportion.

5

- Elements required to measure the process operation

Indicators of volume, when located in particular sectors of the process indicate the raw material provided, and measure the inlet of reactors and take care of gasoil and other compounds outlet.

10

- Level probes

The same are useful to measure the level of the compartments. There is one in the upper part of the main chamber that measures the oil level and another in the chute of the lower compartment that measures the solid level. The pH indicator probe is found at the exit of the turbine while the viscosity indicator probe at the entrance of the turbine.

15

- Temperature indicators

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These are located at the entrance and exit of the turbine, another in the lower part of the main chamber; at the exit of the distillation tower; at the exit of the condenser; and another two that shall measure the entrance and exit temperature of the refrigerating fluid of the condenser.

25

These data shall make it possible to control the process both manually, analogically or digitally.

FINAL TREATMENTS OR TREATMENTS FOLLOWING THE MAIN PROCESS

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In some cases gasoil obtained in the process may be rather shady, and this may be caused by the raw material used or some distortion of the process. Thus there shall be a distillation tower independent from the main process, in which a second distillation shall be carried out, the residues of this process

being returned to the main chamber. The water recollected in the condenser passes by a filter system to settle hydrocarbons dragged by said water. Said hydrocarbons are returned to the main chamber. Later, said water is distilled and is not a problem. In relation to the solids recollected at the end of the main process, if the facility is large enough, there is a possibility to recollect part of the zeolites (if this material is used) which have been precipitated or dragged by inorganic substances. There is raw material such as lignin of the wood which contains a significant higher amount of carbon atoms than hydrogen molecules, which produces a great amount of coke carbon. Coke carbon is later recovered, by separating it from the rest of the solid residues by decantation.

If raw material is rice straw and husk, the silicon contained therein would be recovered. In case of paper slurry silicon, alumina and carbon is recovered. From high sulfured crude, which is useless for conventional distillation, may produce high amounts of sulfur. Many other examples could be mentioned.

Components may be separated from each other by several technologies, and the most suitable shall be applied for each particular case.

20 INDUSTRIAL APPLICATION

The production of liquid hydrocarbons by means of our process shows no difficulties at all.

25 These facilities shall be named SMRF: The components of which are of simple manufacture. The only requirement is a stainless steel boiler, turbines, engines and other elements that may be acquired in any country since there are plenty of manufacturers of these components. The size and production of the same is very diverse, from a few liters to thousands of liters per hour. They do not mean
30 a risk to the environment, and they do not require any external service. Therefore, they may be installed in the same location as the raw material. The physical appearance of the facilities may vary.

Claims:

1. Process to obtain liquid hydrocarbons from the cleavage of material containing carbon and hydrogen as components, that comprises a first physical/mechanical stage and second chemical stage, wherein the process also comprises an initial stage of filling a main chamber and at least one turbine with oil comprising saturated liquid hydrocarbons; in the first physical/mechanical stage the material is first subjected to a controlled temperature until the material reaches 240°C, the material is mixed with oil and with reactants selected to produce exothermic reactions; and grinding of the material occurs in the at least one turbine until the material is reduced to a size of about 20 micron in section; and the second chemical stage is characterized by the addition of sodium- or calcium-based zeolites beads as neutralizers; whereby light hydrocarbons and heavy hydrocarbons are provided at an exit of the at least one turbine as vapour and as liquid respectively.
2. Process in accordance with claim 1, wherein the material containing carbon and hydrogen as components is selected from the group consisting of biomass, hospital residues, urban solid residues, vehicle residues, petrochemical residues, textiles, meat residues, animal fat, leather and manure.
3. Process in accordance with claim 1, wherein the material containing carbon and hydrogen as components is reduced to a 3 mm particle size before being fed to the first physical/mechanical stage.
4. Process in accordance with claim 1, wherein during the first physical/mechanical stage, the size of the material is decreased by self-priming of the at least one turbine, and increasing at the same time the temperature to 270-400°C.
5. Process according to claim 1, comprising the use of industrial equipment including the main chamber and the at least one turbine fed with oil comprising saturated liquid hydrocarbons, at controlled temperature, the main chamber and the at least one turbine serving as conducting agent for a fluid flow of said material containing carbon and hydrogen as components and reactants, wherein viscosity being the limiting property of the fluid flow.