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(54) Titre : PROCEDE DE PRODUCTION DE COMBUSTIBLES A PARTIR DE DECHETS  
(54) Title: METHOD FOR THE PRODUCTION OF FUELS FROM WASTE

(57) **Abrégé/Abstract:**

The invention relates to a method for disposal and reclamation of waste materials of all types, wherein the waste materials are compressed in batches into compact packages and run through temperature treatment zones, to give synthesis gas and the synthesis gas is transformed in a further reaction to give hydrocarbon molecules.



### **Abstract**

The invention relates to a method for the disposal and utilisation of waste materials of all types, in which the waste materials are compressed in batches to form compact packets and pass through temperature treatment zones, synthesis gas being produced, and the synthesis gas is converted in a subsequent reaction into hydrocarbon molecules.

### Method for the production of fuels from waste

The present invention relates to a method in which synthesis gas is produced firstly from waste and the synthesis gas is converted subsequently into hydrocarbons. The hydrocarbons which are produced can be used as fuels.

The development in the oil price in the last few years has continued to go upwards. Even if the oil price falls partly in the interim, a high oil price must be assumed in the long term so that alternative methods for the production of fuel will become of greater interest in the future.

The best known method for the alternative production of fuel is the Fischer-Tropsch synthesis. The Fischer-Tropsch process is an industrial scale method for the conversion of synthesis gas ( $\text{CO}/\text{H}_2$ ) into liquid hydrocarbons which was developed by Franz Fischer and his colleague Hans Tropsch in Mülheim an der Ruhr before 1925. The process was applied on an industrial scale from 1934 by Ruhrchemie

AG. It is a synthesis reaction of CO/H<sub>2</sub> mixtures on iron- or cobalt catalysts to form paraffins, alkenes and alcohols.

The chemical mechanism of the Fischer-Tropsch synthesis reaction (polymerisation) leads mainly to long-chain, only slightly branched (i.e. essentially linear) hydrocarbon molecules. Different chain lengths are found in the product mixture. The chain length range of C<sub>5</sub>-C<sub>20</sub> is of particular interest for the production of fuels. The chain length can be adjusted by choice of catalyst (cobalt, iron, with promoters) and synthesis conditions (above all temperature, synthesis gas composition, pressure). The primary Fischer-Tropsch synthesis products are then processed chemically in the direction of higher fuel yields and qualities (e.g. hydrocracking, isomerisation, i.e. methods of crude oil processing).

Because of the characteristic feature of the chemical synthesis mechanism of forming mainly only slightly branched hydrocarbon molecules, the product is suitable above all as a high-quality diesel fuel with a high cetane number and extremely low contents of sulphur and aromatics. Product mixtures with respect to a different chain length of the hydrocarbons can furthermore be tailor-made with respect to vapour pressure, distillation curves inter alia by applying the highly developed crude oil refinery methods. These synthetically produced diesel fuels have the advantage of being particularly low-pollution and hence environmentally friendly.

At the moment, South Africa is the only country which covers a large part of its fuel requirements by means of the Fischer-Tropsch reaction. The synthesis gas for the synthesis is produced there from coal.

In Germany, the company Choren has developed a method for producing synthesis gas for the first time from biomass with the Carbo-

V process and then fuel (so-called SunDiesel) with the help of the Fischer-Tropsch process. The Carbo-V® process is a three-stage gassing process with the partial processes:

- low temperature gassing,
- high temperature gassing and
- endothermic flue flow gassing

The biomass (water content 15 - 20%) is carbonised in the first process step continuously by partial oxidation (carbonising) with air or oxygen at temperatures between 400 and 500°C, i.e. broken down into tar-containing gas (volatile components) and solid carbon (biocoke).

In the second process step, the tar-containing gas is reoxidised in a combustion chamber above the ash-fusion point of the combustible materials substoichiometrically with air and/or oxygen to form a hot gasification medium.

In the third process step, the biocoke which is ground to form pulverised fuel is blown into the hot gasification medium. Pulverised fuel and gasification medium thereby react endothermally in the gasification reactor to form synthesis crude gas. This can be used then after corresponding conditioning as combustible gas for the production of current, steam and heat or as synthesis gas with the help of the Fischer-Tropsch process for the production of SunDiesel. Disadvantages of this process are that the gasification takes place in several steps and the biocoke must be ground up. In addition, this method is not suitable for gasification of wastes of all types.

It is hence the object of the present invention to provide a method which allows gasification of waste and also subsequent synthesis of fuels, as far as possible the entirety of the waste being able to be used.

According to the invention, a method for the disposal and use of waste materials of all types is provided, in which the waste materials are subjected to a zone-wise temperature impingement and thermal separation or material conversion and the resulting solid residues are converted into a high temperature melt, wherein the waste materials are compressed in batches to form compact packets and pass through temperature treatment zones, with at least one low temperature zone and at least one high temperature zone in which synthesis gas is produced from the disposal material, in the direction of increasing temperature, the produced synthesis gas passes through a gas-permeable bed and also a stabilisation zone for the synthesis gas which is situated above the bed and subsequently is conducted out of the stabilisation zone, the synthesis gas being converted in a subsequent reaction into hydrocarbon molecules. The reaction product preferably concerns fuel, particularly preferred diesel fuel.

An essential advantage of the method is that now waste materials of all types, i.e. waste which is treated, untreated, containing pollutants and hazardous material and also biowaste, can be used without preceding complex separation in the method according to the invention. A method of this type is known in the state of the art as Thermoselect method and is described in more detail for example in the European patents EP 1 187 891 B1, EP 1 252 264 B1, EP 1 377 358 B1, EP 0 790 291 B1 or

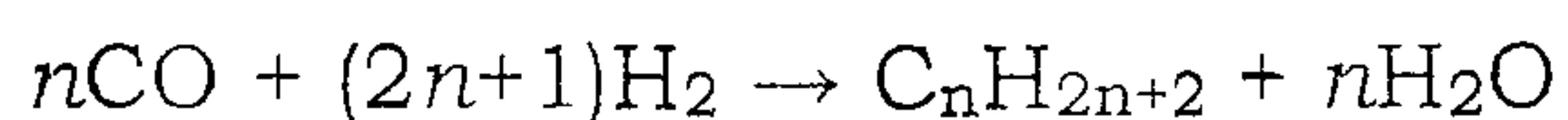
EP 0 726 307 B1.

In an advantageous development, the method provides that at least 70%, preferably 100%, of the produced synthesis gas is used for the reaction into hydrocarbons. The non-used proportion of synthesis gas is thereby used advantageously for covering the inherent energy requirement of the disposal method. This entails the advantage that a neutral energy balance of the method is ensured. Furthermore, it is an essential advantage of the method that a quasi-emission-free course is ensured.

In a further preferred embodiment, the gaseous, liquid and/or solid by-products resulting from the reaction of the synthesis gas into hydrocarbons are returned to the high temperature zone of the synthesis gas production so that the Fischer-Tropsch synthesis can be also implemented without further waste which would require to be disposed of subsequently.

In a further preferred embodiment, the by-products of the Fischer-Tropsch synthesis are used to cover the inherent energy requirement of the disposal method.

In order to achieve good yields, it is favourable if the reaction is implemented in a temperature range of 200°C to 350°C and pressures of 10 - 30 bar according to the general reaction equation



The reaction is known in the state of the art as the Fischer-Tropsch process. Reference is made in this respect to the optimised method

conditions known to the person skilled in the art and mentioned in the state of the art, such as e.g. pressure, temperatures and catalyst systems.

Furthermore, it is advantageous if the method is controlled such that the hydrocarbons have on average 5 to 20 carbon atoms and are as unbranched as possible. With the Fischer-Tropsch synthesis, the synthesis of longer-chain hydrocarbons is also possible in general; longer-chain hydrocarbons, e.g. paraffins, have however too high a melting point to be able to be used as liquid fuel. Hydrocarbons which have on average 5 to 20 carbon atoms are outstandingly suitable however for use as synthetic diesel fuel.

Since the synthesis gas for the Fischer-Tropsch process which is obtained from the gasification method has a relatively unfavourable volume ratio of carbon monoxide to hydrogen, it is advantageous in addition if the volume ratio of carbon monoxide to hydrogen is moved in a shift reaction in favour of hydrogen before the polymerisation reaction. This shift reaction is likewise known to the person skilled in the art from the state of the art; reference is made to the optimised reaction conditions and catalysts used.

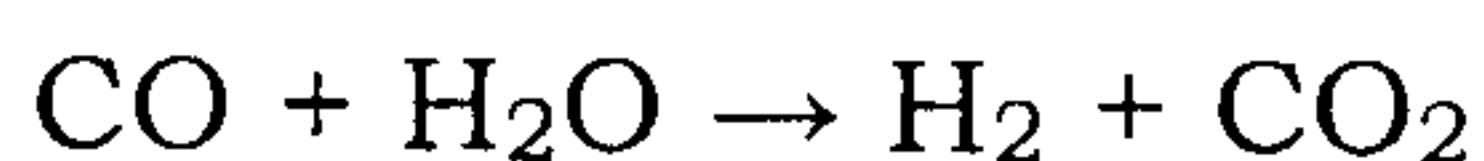
In a further embodiment which is to be preferred, the volume ratio of carbon monoxide to hydrogen is thereby adjusted in the shift reaction to at least 1 to 1.5, preferably at least 1 to 2.

In addition, a use of the above-described method is indicated with the present invention. According to the invention, the method can be used for the synthesis of fuels, preferably for the synthesis of diesel fuels.

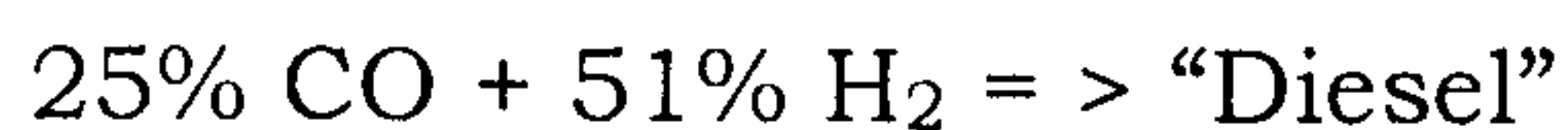
The method according to the invention is explained subsequently in more detail with reference to an example without wishing to restrict the invention to the method parameters used there.

### **Example for method control**

The method according to the invention is explained in more detail with reference to a Thermoselect plant which has two lines with respectively 15 t/h waste throughput, i.e. in total allows 30 t/h waste throughput. An average waste calorific value of 12 MJ/kg waste is thereby the basis of the operation. In the case of continuous operation of the plant, approx. 30,000 Nm<sup>3</sup>/h synthesis gas of the composition 38% by volume CO, 38% by volume H<sub>2</sub> and 14% by volume CO<sub>2</sub> can thereby be obtained. The fuel production is effected according to the Fischer-Tropsch process. In order to set a CO/H<sub>2</sub> ratio which is favourable for the Fischer-Tropsch reaction, a part of the CO is converted to form H<sub>2</sub> in a shift reaction. The CO<sub>2</sub> resulting hereby is separated.



13% CO of the 38% CO in the synthesis gas are converted in the shift reaction, i.e. after the shift reaction, a synthesis gas with 25% CO and 51% H<sub>2</sub> is obtained, which is used then in the Fischer-Tropsch synthesis. The synthesis gas which has thus been enriched with hydrogen and brought to a ratio of CO to H<sub>2</sub> which is favourable for the Fischer-Tropsch reaction is now polymerised into diesel fuel



60% of the synthesis gas used were achieved as yield over all the steps of the fuel production. This is very close to the value in the literature

which indicates 75% for an optimised method under laboratory conditions. The specific volumetric weights of CO and hydrogen were the basis for the calculation of the material balance. The equation is indicated in the following

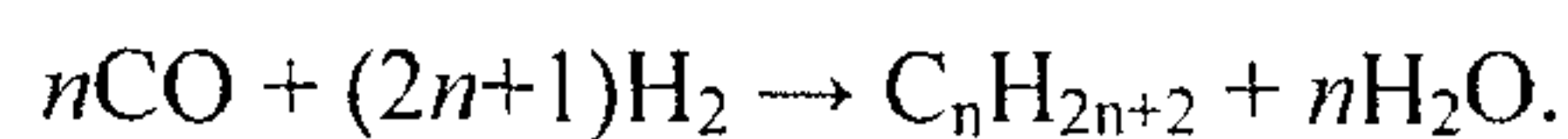
$$21,000 \text{ m}^3/\text{h} (0.25 \cdot 1.258 \text{ kg/m}^3 + 0.51 \cdot 0.089 \text{ kg/m}^3) = 7557 \text{ kg/h}$$

In the case of an average density of 0.83 kg/l of the synthetic diesel, a quantity of 7,800 l/h diesel is hence produced. With a 2-line Thermoselect plant, 7,800 litres of diesel can therefore be produced per hour.

The embodiments of the present invention for which an exclusive property or privilege is claimed are defined as follows:

1. A method for forming hydrocarbons from waste materials, in which the waste materials are subjected to a zone-wise application of temperature and material conversion and resulting solid residues are converted into a high temperature melt, said method comprising the steps of: compressing the waste materials in batches to form compact packets and passing through temperature treatment zones, with at least one low temperature zone and at least one high temperature zone in which synthesis gas is produced from the waste material in a direction of increasing temperature; passing the produced synthesis gas through a gas-permeable bed and also a stabilisation zone for the synthesis gas which is situated above the bed; conducting the synthesis gas out of the stabilisation zone; and converting only a portion of the synthesis gas in a subsequent reaction into hydrocarbon molecules, wherein energy inherent in the portion of the synthesis gas not used for the reaction is used for covering an inherent energy requirement of the method.
2. The method according to claim 1, wherein at least 70% of the produced synthesis gas is used for the reaction into hydrocarbons.
3. The method according to claim 1, wherein at least 80% of the produced synthesis gas is used for the reaction into hydrocarbons.
4. The method according to any one of claims 1 to 3, wherein at least one of gaseous, liquid and solid by-products resulting from the reaction are returned to the at least one high temperature zone of the synthesis gas production.
5. The method according to claim 4, wherein the returned by-products are used to cover an inherent energy requirement of the method.

6. The method according to any one of claims 1 to 5, wherein the reaction is implemented in a temperature range of 200°C to 350°C according to the general reaction equation



7. The method according to any one of claims 1 to 6, wherein the hydrocarbons have on average 5 to 20 carbon atoms.
8. The method according to any one of claims 1 to 7, wherein a volume ratio of carbon monoxide to hydrogen of the synthesis gas is moved in a shift reaction in favour of hydrogen before the reaction.
9. The method according to claim 8, wherein the volume ratio of carbon monoxide to hydrogen is at least 1 : 1.5 after the shift reaction.
10. Use of the method according to any one of claims 1 to 9 for synthesis of fuel.
11. The use according to claim 10, wherein the fuel is diesel fuel.