

12 **EUROPEAN PATENT APPLICATION**

21 Application number: **86200283.9**

22 Date of filing: **24.02.86**

51 Int. Cl.4: **C 07 C 1/04, C 07 C 27/06,**  
**C 07 C 29/15, C 07 C 31/04**  
**// B01J8/02**

30 Priority: **28.03.85 NL 8500910**

43 Date of publication of application: **01.10.86**  
**Bulletin 86/40**

84 Designated Contracting States: **DE FR GB IT NL**

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54 **Process for the preparation of organic compounds from synthesis gas.**

57 Process for the preparation of organic compounds from synthesis gas by passing said gas in at least one reaction zone through fluid-permeable holders containing catalyst particles which holders are stacked in the reaction zone(s).

**EP 0 196 124 A1**

PROCESS FOR THE PREPARATION OF ORGANIC  
COMPOUNDS FROM SYNTHESIS GAS

The invention relates to a process for the preparation of organic compounds from synthesis gas.

In this method of preparation, in which synthesis gas is led continuously or discontinuously through a catalyst bed, it is often  
5 desirable to employ as small catalyst particles as possible in order to improve the yield per unit weight of catalyst. It is not, however, possible to reduce the particle size of the catalyst indefinitely, since the pressure drop in a catalyst bed in the direction of flow of the synthesis gas is greater as the catalyst  
10 particles are smaller. The greater pressure drop often cancels out the advantage ensuing from the employment of smaller particles.

It has now been found that the drawbacks connected with the employment of smaller catalyst particles can largely be overcome by employing catalyst particles packed in stacked catalyst holders  
15 permeable to fluid (i.e. gas and liquid).

The invention therefore relates to a process for the preparation of organic compounds from synthesis gas wherein said gas is passed in at least one reaction zone through fluid-permeable holders containing catalyst particles which holders are stacked in  
20 the reaction zone(s).

The process according to the invention causes only a relatively small pressure drop while the yield per unit weight of catalyst remains almost the same as that obtained by employing similar catalyst particles without said holders; in addition mass  
25 transport limitations arising from the employment of larger catalyst particles are largely eliminated. Moreover, heat transfer is improved.

The process according to the invention can be carried out continuously or discontinuously; preferably a continuous process is  
30 employed.

The particle size of the catalyst is preferably between 0.1 and 1.5 mm and more preferably between 0.25 and 1.0 mm, always based on the largest diameter of each particle.

The catalyst holder can in principle have any shape. Preferably, the height and width of the catalyst holder do not differ by more than 50% from the length; in particular, the catalyst holder has a regular shape, for example substantially cylindrical or spherical. Substantially spherical catalyst holders are the most preferred. The diameter of the catalyst holder is advantageously between 2 and 10 mm and in particular between 4 and 8 mm, always based on the largest diameter of each holder.

The catalyst holder suitably consists of a continuous network of material which, under the conditions under which the synthesis gas is contacted with the catalyst, is inert. Preferably, the catalyst holder consists of a closed network of aluminium or stainless steel.

Advantageously 20-95% and preferably 40-90% of the surface area of the holder consists of a permeable area. The permeable area is formed by a plurality of openings in e.g. a network, which openings have a diameter of 0.05 to 0.7 mm and in particular of 0.1 to 0.5 mm, the diameter of course always being chosen such that the catalyst particles in the catalyst holder cannot pass through the openings in the catalyst holder.

At least 50%, preferably at least 80% and in particular the entire volume of the reaction zone is occupied by the stacked catalyst holders forming interstices, the interstices between the stacked catalyst holders preferably occupying between 20 and 50% of the volume in the reaction zone.

The process according to the invention is in principle suitable for any conversion of synthesis gas into organic compounds. In such a conversion, the synthesis gas is passed at a particular temperature and pressure and with a particular space velocity through a catalyst bed containing a particular catalyst packed in the above-described catalyst holders. The choice of

catalyst, temperature, pressure and space velocity depends on the desired product.

5 The process according to the invention is particularly suitable for the preparation of hydrocarbons and/or oxygen-containing hydrocarbon derivatives, such as methanol, from synthesis gas.

10 If the process according to the invention is carried out for the preparation of methanol, catalysts known in the art for converting synthesis gas into methanol should be employed as catalyst, e.g. a catalyst containing zinc together with chromium.

15 If the process according to the invention is carried out for the preparation of hydrocarbons, Fischer-Tropsch catalysts known in the art, which contain Fe, Co, Ru and/or Ni, can be employed. The present invention is suitable for the preparation of middle distillates. In this context, "middle distillates" are understood to be hydrocarbon mixtures whose boiling range corresponds substantially to that of the kerosine and gas oil fractions, which are obtained in the classical atmospheric distillation of crude petroleum. The middle distillate range extends substantially from about 150 to 360 °C.

20 Middle distillates can be prepared in one or two stages. They are prepared in one stage by passing the synthesis gas over a Fischer-Tropsch catalyst with one or more promoters and a carrier material. The products which can be prepared with these catalysts generally contain a very wide molecular weight distribution and, in addition to branched and non-branched paraffins, often contain considerable quantities of olefins and oxygen-containing organic compounds. The products obtained often contain only a small proportion of middle distillates. Besides the yield, the product characteristics of the gas oil obtained leave much to be desired as a consequence of the presence of the previously mentioned olefins and oxygen-containing organic compounds. That is why the two-stage method of preparation is preferably used, in which in a first step a class of Fischer-Tropsch catalysts is used, which catalysts have the property that they give a product containing only very small

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amounts of olefins and oxygen-containing organic compounds and consisting almost exclusively of non-branched paraffins, a large proportion of which boil above the middle distillate range, and in which in a second stage the high-boiling part of the product  
5 obtained in the first stage is converted by hydrocracking into middle distillates. As feedstock for the hydrocracking, at least that part of the product is chosen whose initial boiling point lies above the final boiling point of the heaviest middle distillate desired as end product. The hydrocracking, which is characterized  
10 by a low hydrogen consumption, gives middle distillates with a substantially better pour point than those obtained from the direct conversion of a  $H_2/CO$  mixture according to the Fischer-Tropsch method.

The process according to the invention is advantageously  
15 employed in the first stage of this two-stage method of preparation.

The Fischer-Tropsch catalysts used in the first stage of the two-stage method of preparation preferably contain silica, alumina or silica-alumina as carrier material, and cobalt together with  
20 zirconium, titanium and/or chromium as catalytically active metals, preferably in such quantities that 3-60 parts by weight cobalt and 0.1-100 parts by weight zirconium, titanium and/or chromium are present per 100 parts by weight carrier material. The catalysts are advantageously prepared by kneading and/or impregnating the metals  
25 in question onto the carrier material. Before being used, the cobalt catalysts are preferably activated. This activating can be suitably carried out by contacting the catalyst at a temperature of between 200 and 350 °C with hydrogen or a hydrogen-containing gas.

The conversion of synthesis gas into middle distillates is  
30 preferably carried out at a temperature of 125-350 °C and in particular of 175-275 °C and a pressure of 5-100 bar and in particular of 10-75 bar.

The  $H_2$ - and CO-containing feedstock, which is converted into middle distillates with the aid of the above-mentioned catalysts,

preferably has an  $H_2/CO$  mol. ratio of 1.0-2.5 and in particular of 1.5-2.25.

Although in the preparation of middle distillates from the product obtained via the synthesis catalyst, that part of the product whose initial boiling point lies above the final boiling point of the heaviest middle distillate desired as end product can be used as feedstock for the hydrocracking, use is preferably made for this purpose of the total  $C_9+$  fraction and in particular of the total  $C_5+$  fraction of the product of the first stage, since it has been observed that under the influence of the catalytic hydrogen treatment, the quality of the gasoline, kerosine and gas oil fractions contained therein is improved.

The hydrocracking is carried out by contacting the fraction to be treated, at elevated temperature and pressure and in the presence of hydrogen, with a catalyst containing one or more noble metals from Group VIII on a carrier. As hydrocracking catalyst, a catalyst is preferably employed which contains 0.1-2 wt% and in particular 0.2-1 wt% of one or more noble metals from Group VIII on a carrier. Preferred catalysts are those which contain platinum or palladium as noble metal from Group VIII and silica-alumina as carrier. The hydrocracking is preferably carried out at a temperature of 200-400 °C and in particular of 250-350 °C and at a pressure of 5-100 bar and in particular of 10-75 bar.

If the reaction product prepared via the synthesis catalyst still contains sufficient unconverted hydrogen for carrying out the hydrocracking, both steps can be carried out in "series flow". In that case, the  $C_8-$  fraction or the  $C_4-$  fraction is not separated after the first stage, but only after the second stage. As is known, carrying out a multi-stage process in series flow means that the total reaction product from a given stage, without components being removed from it or added to it, is used as feedstock for the following stage, which is carried out substantially at the same pressure as the previous stage.

The invention will now be illustrated with the aid of the following Examples of which only Example 3 relates to the process according to the invention.

Comparative Example 1

5           Synthesis gas (molar ratio  $H_2 : CO = 2$ ) was contacted at 230 °C and 20 bar and at a space velocity of 900 l (STP)/l catalyst/hour with 8 kg catalyst (9 parts by weight cobalt and 6 parts by weight zirconium per 100 parts by weight  $SiO_2$  as carrier) in a reactor with a volume of 13 l. The catalyst consisted  
10 of catalyst particles with a diameter of 0.38 mm.

Comparative Example 2

Example 1 was repeated, except that the diameter of the catalyst particles was now 2.4 mm.

Example 3

15           Example 1 was repeated, except that the catalyst particles were packed in catalyst holders. The catalyst holders were spherical, had a diameter of 6 mm and consisted of a network of stainless steel with openings of 0.3 mm and a permeable area of 75% of the network area. The reactor was, except for the interstices,  
20 entirely filled with catalyst holders. The quantity of catalyst was 5.2 kg.

          In these 3 Examples the yield (expressed as  $kg C_1+.kg$  catalyst<sup>-1</sup>.h<sup>-1</sup>) the selectivity (the part of the  $C_1+$  fraction that belonged to the  $C_3+$  fraction) and the pressure drop were  
25 determined.

The results are given in Table 1 below.

Table 1

Example	1	2	3
diameter of catalyst particles	0.38 mm	2.4 mm	0.38 mm
catalyst holder	-	-	+
yield	123	52	120
selectivity (C <sub>3</sub> +/C <sub>1</sub> +) .	87	67	83
pressure drop (bar)	10	0.25	0.04



C L A I M S

1. Process for the preparation of organic compounds from synthesis gas wherein said gas is passed in at least one reaction zone through fluid-permeable holders containing catalyst particles which holders are stacked in the reaction zone(s).
- 5 2. Process according to claim 1 wherein the catalyst particles have a diameter lying between 0.1 and 1.5 mm.
3. Process according to claim 1 or 2 wherein the catalyst holders have a width and height not differing by more than 50% from the length.
- 10 4. Process according to any of the preceding claims wherein the catalyst holders are substantially cylindrical or spherical.
5. Process according to any of the preceding claims wherein the catalyst holders have a diameter lying between 2 and 10 mm.
- 15 6. Process according to any of the preceding claims wherein the interstices between the stacked catalyst holders occupy between 20 and 50% of the volume in the reaction zone.
- 20 7. Process according to any of the preceding claims wherein the catalyst holders consist of a continuous network of material which is inert under the conditions under which the synthesis gas is contacted with the catalyst.
8. Process according to claim 7 wherein the catalyst holders consist of a closed network of aluminium or stainless steel.
- 25 9. Process according to any of the preceding claims wherein between 20 and 95% of the surface area of the holders consists of permeable area.
10. Process according to any of the preceding claims wherein the holders are provided with openings having a diameter lying between 0.1 and 0.5 mm.
- 30 11. Process substantially as described hereinbefore with reference to Example 3.

CXRH04



DOCUMENTS CONSIDERED TO BE RELEVANT			EP 86200283.9
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	US - A - 4 289 855 (WHITLEY) * Claims * --	1,8	C 07 C 1/04 C 07 C 27/06
X	US - A - 4 215 011 (SMITH, JR.) * Claims * --	1,8	C 07 C 29/15 C 07 C 31/04 //B 01 J 8/02
X	GB - A - 2 077 136 (ATOMIC ENERGY AUTHORITY) * Page 1, lines 10-56; page 2, lines 37-76; claims * --	1,3,4	
A	US - A - 4 276 265 (GILLESPIE) * Claims * --	1,8	
A	CATALYSIS - SCIENCE AND TECHNOLOGY, vol. 1, 1981 Springer-Verlag, Berlin, Heidelberg pages 162-164 * Page 162, line 21 - page 164, line 21 * --	1	<b>TECHNICAL FIELDS SEARCHED (Int. Cl.4)</b> C 07 C 1/00 C 07 C 27/00 C 07 C 29/00 C 07 C 31/00
A	DE - B - 1 668 390 (METALLGESELLSCHAFT AG) * Claim 1 * ----	1	B 01 J
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 23-05-1986	Examiner KÖRBER
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			