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(54) Title: METHOD IN THE PRODUCTION OF METHYL FORMATE AND METHANOL IN A LIQUID PHASE

(57) Abstract

A method in the production of methyl formate and methanol from a syngas comprising carbon monoxide and hydrogen in one reaction step, the reaction being carried out catalytically in a liquid phase mainly consisting of methanol, simultaneously with continuous removal of methyl formate and methanol from the reaction as a gas.

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METHOD IN THE PRODUCTION OF METHYL FORMATE AND METHANOL IN A LIQUID PHASE.

The present invention relates to a process for the production of methyl formate and methanol from carbon monoxide and hydrogen - so-called syngas.

The production of methyl formate and methanol is carried out in one step and is catalyzed by a system of catalysts comprising an alkali or earthalkali metal alcoholate and a heterogeneous Cu, Cr catalyst. The reaction occurs in a liquid phase.

Methanol and methyl formate are formed by a chemical reaction of carbon monoxide and hydrogen according to the following total reactions:

I.	CO carbon monoxide	$+ 2 H_2$ hydrogen	CH_3OH methanol
II.	$2 CO$ carbon monoxide	$+ 2 H_2$ hydrogen	$HCOOCH_3$ methyl formate

It is previously known to provide methyl formate from methanol and carbon monoxide in the presence of an alkali or earth alkali metal alcoholate (cf. DE-AS 1 147 214, Norw. Specification 135 749), nad it is, furthermore, known that methanol can be produced by hydrogenolysis of methyl formate. DE-PS 902 375, thus, indicates a method, wherein methyl formate and hydrogen are reacted in a catalytic gas phase reaction to form methanol.

It is, furthermore, known to manufacture methyl formate and methanol in a catalytic gas phase reaction at elevated temperatures, although this has not been utilized for industrial production at a large scale.

Also, it has been suggested to carry out the reactions I and II in one and the same step (cf. DE-PS 809 803), where the formation of methanol is indicated. This method has not been utilized industrially so far, since the catalyst systems stated have low productivity and are rapidly deactivated. Industrial production of methanol to day is carried out by a catalytic gas phase reaction of carbon monoxide and hydrogen by the aid of a heterogeneous metal catalyst. The reaction takes place at a pressure of approx. 100 atm. and a temperature of approx. 250°C. The gas phase reaction has the disadvantage that relatively large amounts of gas must be recompressed and resirculated to the reactor, the conversion in each passage through the reactor is relatively low. This disadvantage is strongly enhanced by the fact that the cost of energy is rapidly increasing.

The object of the invention is characterized by the features stated in claim 1.

In connection with the present invention it was surprisingly found that the product methyl formate together with methanol are advantageously removed from the reaction zone as a gas simultaneously with their formation by the chemical reaction in the liquid phase. This fact indicates that methanol is not formed <u>via</u> methyl formate as an intermediate product as conventionally assumed, but rather by a reaction which is independent of the methyl formate concentration, even though the mechanism of such reaction is not known.

The principle of driving-off produced methanol/methyl formate from the reactor brings several advantages, technically speaking, which are so important that they will make the process technically/economically competitive.

The chemical reactions taking place at the formation of methyl formate and methanol involves the liberation of considerable quantities of heat. Since the process i.a. requires defined temperatures in the reactor, heat must be removed from the zone of reaction. The reaction occurring in a liquid phase, this can be done in a simple and efficient manner as compared to a gas phase reactor. As the product, furthermore, is driven off from the liquid phase and removed from the reactor together with non-reacted carbon monoxide and hydrogen, the reaction heat will gradually be compensated by loss of heat due to the evaporation of reaction products. As regards heat economy, this is very advantageous, since the quantities of energy that would otherwise be necessary in the reactor for cooling, can thus be reduced. The evaporation of the product also in an advantageous manner renders it possible to achieve an indirect heat control of the process by varying the amount of driven off product, since the temperature of the reactor can be adjusted in this manner.

By removing the product as a gas process technical advantages associated with the catalyst, its activity and lifetime and and its handling in the process are also achieved. The catalyst, which is present as suspended material and dissolved salt (alcoholate) in the reaction medium, will not be removed, but on the contrary remain in the reactor when the product is driven off. This means the elimination of any necessary separation to remove catalyst from product in case the product had been removed from the reactor in the liquid phase. The catalyst can, thus, be handled via a separate process flow for any desired supply of fresh or regeneration of used catalyst.

In connection with the present invention it was also surprisingly found that there is a connection between the lifetime of the catalyst and the utilization of the principle of driving off the products from the reaction medium. The principle of driving off methyl formate from the reaction medium can, thus, suitably be utilized to minimize the concentration of methyl formate in order to increase the lifetime of the catalyst.

The reaction according to the invention occurs in a liquid reaction phase in the presence of an alkali or earth alkali alcoholate, preferably an alcoholate formed from methanol, and a heterogeneous catalyst comprising a Cu-Cr oxide compound suspended in the liquid reaction mixture. The pressure and the temperature of the reaction may be varied within wide limits. Preferably, pressures from 10 to 100 bar are used. The temperature is chosed to achieve a practical rate of the reaction. Preferably, the reaction is carried out at a temperature in the range of 50°C to 240°C.

It is known to produce "copper chromite" catalysts by calcination of a chemical compound with an approximate composition $Cu(OH)\ (NH_4)CrO_4$ in the presence of air at a temperature of approximately 350°C and subsequent reduction of the product with hydrogen. Copper chromite catalysts of said kind may be utilized in the process, but according to the present invention it proved especially suitable to utilize spesific Cu-Cr oxide catalysts, which are produced when the above mentioned calcination process in air instead is carried out in an inert atmosphere, e.g. argon, helium, nitrogen or similar inert gases, and is subsequently reduced with hydrogen according to known methods. It is not known in detail what chemical changes occur to the catalyst during thermal decomposition in an inert atmosphere as compared to the known method of calcination. The thermal decomposition of $Cu(OH)\ (NH_4)CrO_4$ in an inert atmosphere can be carried out at a temperature in the range of 250-500°C, most suitably in the range of 270-320°C.

In addition to the above mentioned Cu-Cr oxide component, the catalyst system can naturally also comprise other components or carriers conventionally utilized in connection with heterogeneous hydrogenation catalysts, as for instance ZnO, Al_2O_3, Fe_2O_3, MnO, MgO, CaO. BaO, SiO_2, activated carbon and the like.

The reaction occurs in a technical reactor that is known for solid/liquid phase/gas systems. Preferably a kind of reactor is chosen that is characterized by good mixture of gas/liquid /solids. In the reaction methyl formate as well as methanol are formed, and the ratio between said components in the product can be varied within wide limits by changing the process conditions and the composition of the catalyst.

Methanol naturally functions as a solvent for the reaction. Other organic solvents, as for instance higher alcohols, ether, saturated hydrocarbons and aromatics could also be utilized. A syngas free of water, sulphur and CO_2, and wherein the molar ratio of carbon monoxide and hydrogen can be varied, is used in the present method.

On account of the conversion rate as well as the selectivity regarding the conversion to the desired products it is critical that the reaction takes place in an approximately anhydrous reaction medium.

Methyl formate and methanol are recovered as top and bottom products respectively in a separation column. Part of the produced amount of methanol is suitably returned to the reactor. The produced methanol has an especially high degree of purity (approximately anhydrous) and is, thus, especially well suited for this object. A sketch of such an embodiment of the process is shown in Figure 11.

The present invention represents an advantageous and very flexible process alternative for coproduction og methyl formate and methanol. The product composition may vary from pure methyl formate to pure methanol, and it is possible to control production according to the actual state of the market at any time. The prospects of the market of methanol as well as methyl formate are very promising, as will be known. The characteristics of methanol are studied with a view to future utilization of methanol as an energy carrier.The expected and considerable increase in production because of this will involve the need of additional plants with larger throughput. Thus, there should be a demand as well as good chances of adapting novel and improved process technology for methanol production in an industrial scale.

Methyl formate seems to become an essential intermediate in C_1-based chemistry, since it is reasonably priced for utilization as a raw material for a series of essential petrochemical products.

The following examples will further illuminate the object of the present invention.

Examples 1 - 9

The reaction of carbon monoxide and hydrogen was studied in two essentially different reactor systems. It is common to both systems that the reaction occurs in one step in the presence of a catalyst system consisting of an alkali or earth alkali metal alcoholate and a Cu-catalyst.For both systems a micro reactor with a volume of 120 ml was used.

In one reactor system formed methyl formate and methanol are removed from the reactor by bubbling an excess of carbon monoxide and hydrogen through the reactor. In this case the products are removed as gases. The amount of gas is adjusted to keep a constant liquid level. In this case the catalyst remains in the reactor. The results are shown by graph I in the Figures 1-9.

In the other reactor system formed methyl formate and methanol are removed from the reactor in the liquid phase, so that dissolved and suspended catalyst is carried with the product flow from the reactor. Heterogeneous catalyst is recovered in a hydrocyclone and is pumped back to the reactor. Methanol and methyl formate are flashed by the product flow in a separation zone and recovered homogeneous catalyst is recirculated to the reactor. The results are shown in graph II of Figures 1-9.

The activity of the catalyst system as a function of time is shown for various compositions of pressure, temperature and catalyst. As a heterogeneous catalyst a commercially available catalyst from Girdler-Südchemie Katalysator GmbH, Munich, labelled "G 89" with the nominal composition: 39% Cu, 32% Cr, and 2,5% Mn was used in all tests. The activity is given as kg produced methanol per kg catalyst (alcoholate) per time unit, and the results are shown in the attached diagrammes. The results clearly show that the catalyst activity declines slower when the reaction products are removed in the gas phase and not the liquid phase.

Example 10

Small portions of Cu (OH) NH_4CrO (approx. 2 g) were termally decomposed in an inert atmosphere (He). The sample was kept at maximum decomposition temperature as stated in Figure 10 for one hour. Simultaneously 120 ml/min of helium were passed through the decomposition zone. 0,75 g of the decomposed product in 12 g methanol were then prereduced with hydrogen in a micro autoclave having a volume of 30 ml and provided with magnetic stirring and temperature control at $185^{\circ}C$ and 100 bar hydrogen. After 16 hours the mixture was cooled to $20^{\circ}C$ and the catalyst was separated from the methanol by centrifugation. The catalyst remained in the autoclave whereas the methanol was removed. The autoclave was then supplied with 10 g dried methanol containing 1 mole % Na methylate as catalyst 1. The conversion of carbon monoxide and hydrogen was then carried out at $130^{\circ}C$ and 75 bar for 2,5 hours. After the test the reaction mixture was cooled to $20^{\circ}C$ and analysed by gas/liquid chromatography (glc). The formation of methanol and methyl formate (indicated as % of weight increase) as a function of maximum decomposition temperature is shown by graph I in Figure 10. The selectivity of the reaction of CO and H_2 to methanol/methyl formate was more than 95% in all these tests.

For comparison $Cu(OH)NH_4CrO$ was calcinated in air according to the known methods and tested as a catalyst for the reaction of carbon monoxide and hydrogen according to the same method as stated above. The results are shown by graph II in Figure 10.

The results show that a catalyst that is more active in an substantial degree is provided by thermal decomposition of $CU(OH)NH_4$ in an inert atmosphere, as compared to the activity achieved by known processes of calcination.

CLAIMS:

1. A method for the production of methyl formate and methanol from a syngas comprising carbon monoxide and hydrogen in one reaction step, characterized in that the reaction occurs catalytically in a liquid phase mainly consisting of methanol, simultaneously with continuous removal of methyl formate and methanol from the reaction zone as a gas.

2. A method as stated in claim 1, characterized in that methyl formate and methanol are separated by fractional distillation, whereafter all or part of the methanol is recirculated to the reaction step.

3. A method as stated in claims 1-2, characterized in that the catalytical reaction is carried out in the presence of a catalyst system comprising an alkali or earth alkali alcoholate and a specific Cu-catalyst provided by thermal decomposition of $Cu(OH)(NH_4)CrO_4$ in an inert atmosphere.

4. A method as stated in claims 1-3, characterized in that the reaction is carried out at a temperature below 240°C and a pressure below 100 bar.

AMENDED CLAIMS

[received by the International Bureau on 13 April 1983 (13.04.83);
original claims 1 to 4 replaced by new claims 1 to 7]

1. A method for the production of methyl formiate and methanol by reacting gases containing carbon monoxyde and hydrogen in the presence of a catalyst system consisting of a metal alcoholate and a copper-chrome oxyde, characterized in that methanol and methyl formiate in a liquid phase are co-produced in one reaction step and removed in a gaseous phase from the reaction zone.

2. A method as stated in claim 1, characterized in that methyl formiate and methanol are separated by fractional distillation, whereafter all or part of the methanol is recirculated to the reaction step.

3. A method according to claim 1, characterized in that as metal alcoholate is used barium methoxyde.

4. Method according to claim 1, characterized in that in addition to methanol and methyl formiate an organic inert solvent is present in the liquid phase.

5. Method according to claim 1, characterized in that as copper-chrome oxyde catalyst is used a particular type prepared by thermal decomposition of $Cu(OH)(NH_4)CrO_4$ in an inert atmosphere.

6. Method according to the claims 1-5, characterized in that the reaction is effected at a temperature below 240°C and at a pressure below 100 bar.

7. Cu-Cr oxyde catalyst, characterized in that it is obtained by thermal decomposition of $Cu(OH)(NH_4)CrO_4$ in an inert atmosphere at a temperature below 320°C.

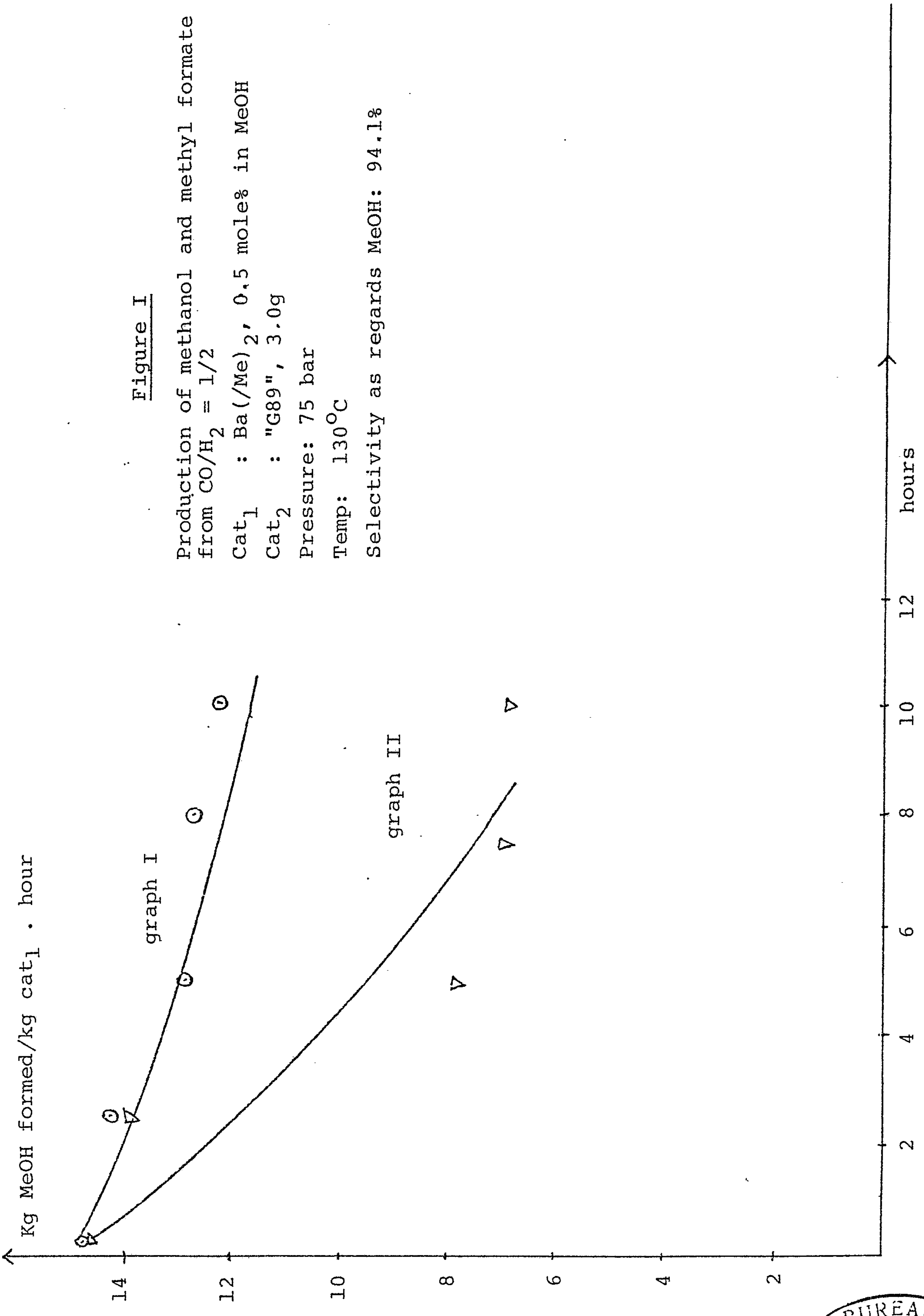


Figure I

Production of methanol and methyl formate from $CO/H_2 = 1/2$

Cat_1 : Ba(/Me)$_2$, 0.5 mole% in MeOH

Cat_2 : "G89", 3.0g

Pressure: 75 bar

Temp: 130°C

Selectivity as regards MeOH: 94.1%

Figure 2

Production of methanol and methyl formate from $CO/H_2 = 1$

Cat_1 : $Ba(OMe)_2$, 0.5 mole % in MeOH

Cat_2 : "G89", 3.0 g

Pressure: 68 bar

Temp. : 150°C

Selectivity as regards MeOH : 99%

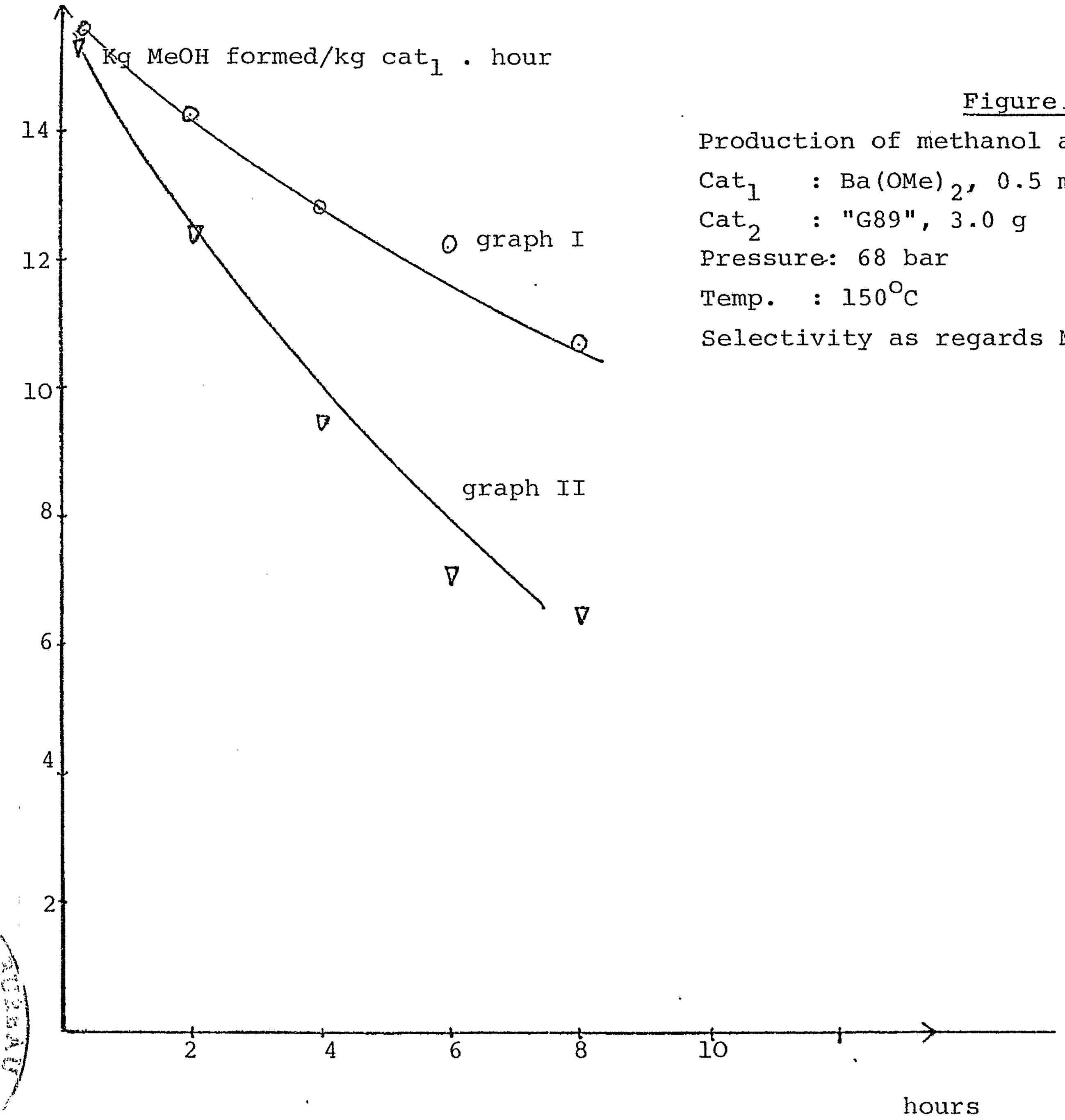


Figure 3

Production of methanol and methyl formate from $CO/H_2 = 1/2$

Cat_1 : Na(OMe), 1.0 mole% in MeOH

Cat_2 : "G89", 3.0 g

Pressure : 75 bar

Temp. : 130°C

Selectivity as regards MeOH : 87.9 %

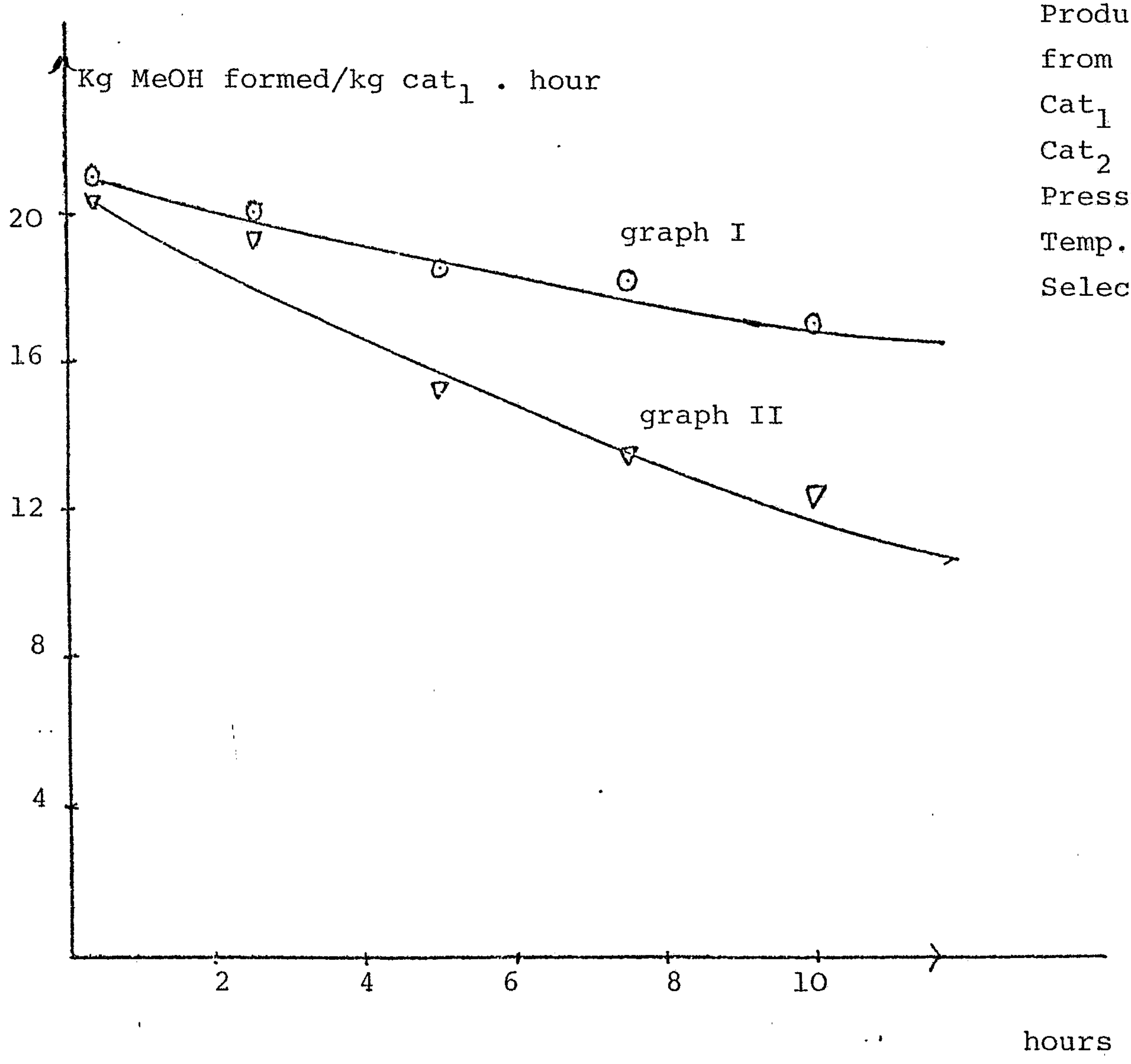


Figure 4

Production of methanol and methyl formate from $CO/H_2 \doteq 1/2$

Cat_1 : Na(OMe), 5.0 mole % in MeOH

Cat_2 : "G89", 3.0

Pressure : 75 bar

Temp. : 130°C

Selectivity as regards MeOH : 94.1

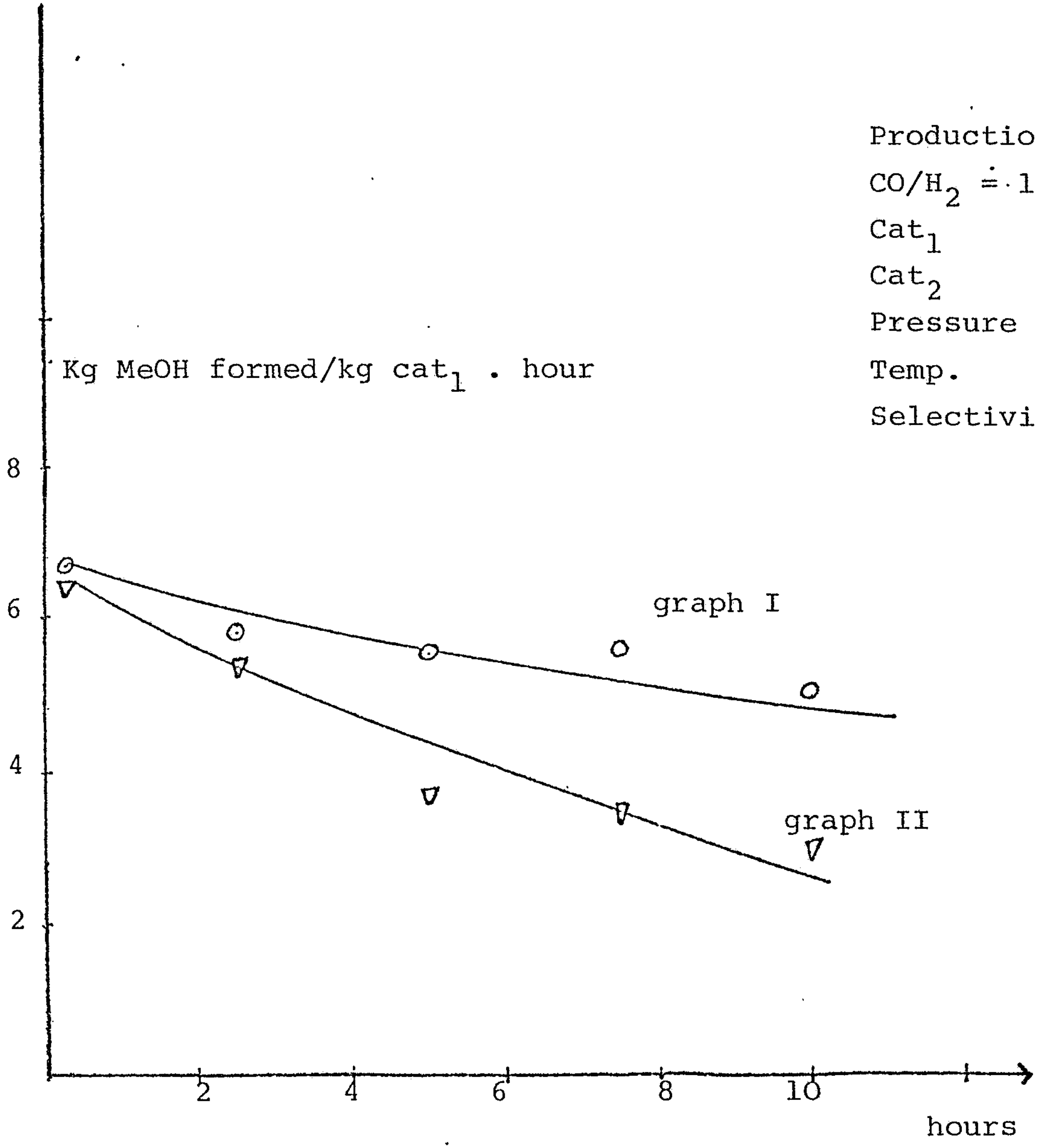


Figure 5

Production of methanol and methyl formate from $CO/H_2 = 1/2$

Cat_1 : Na(OMe), 10.0 mole % in MeOH

Cat_2 : "G89", 1.2 g

Pressure : 75 bar

Temp. : 130°C

Selectivity as regards NeOH : 70.2 %

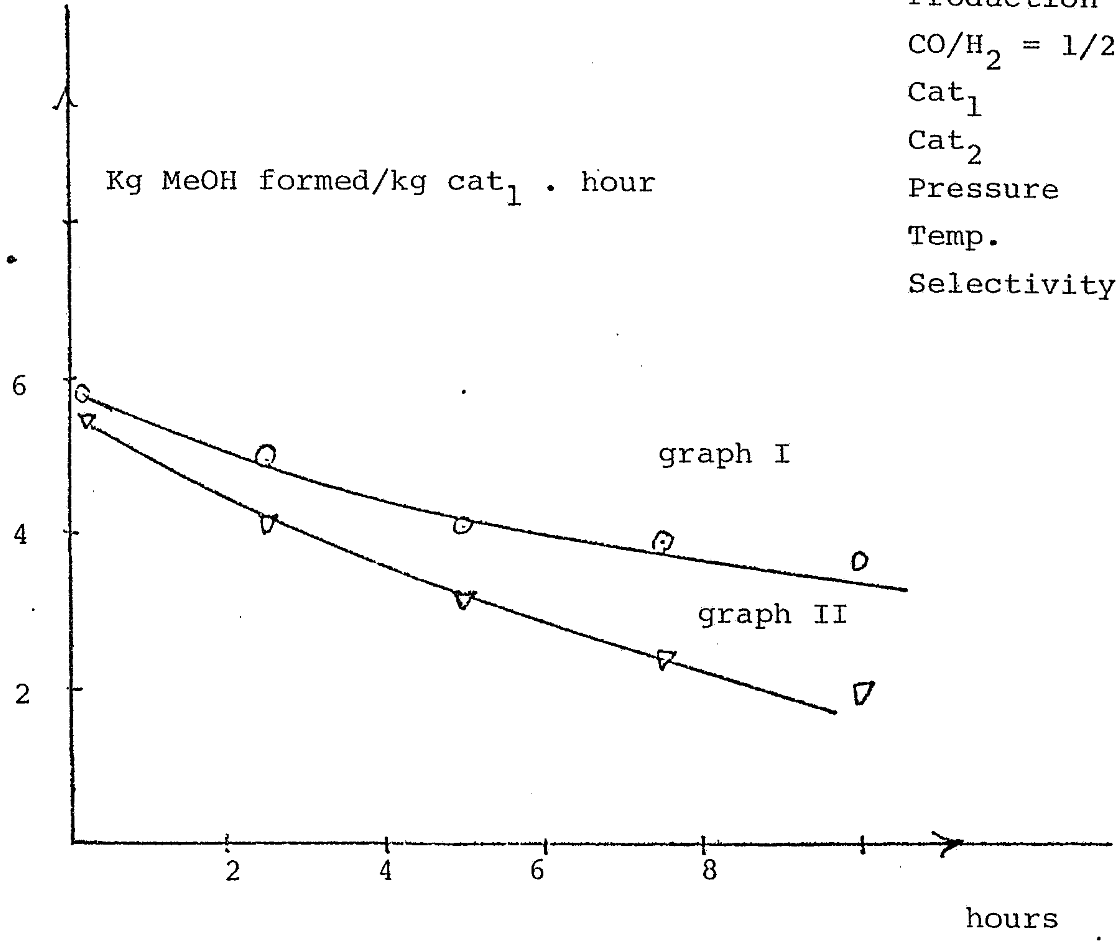


Figure 6

Production of methanol and methyl formate from $CO/H_2 = 1/2$

Cat_1 : Na(OMe), 1.0 mole % in MeOH

Cat_2 : "G89", 3.0 g

Pressure : 80 bar

Temp: : 90°C

Selectivity as regards MeOH: 50.5 %

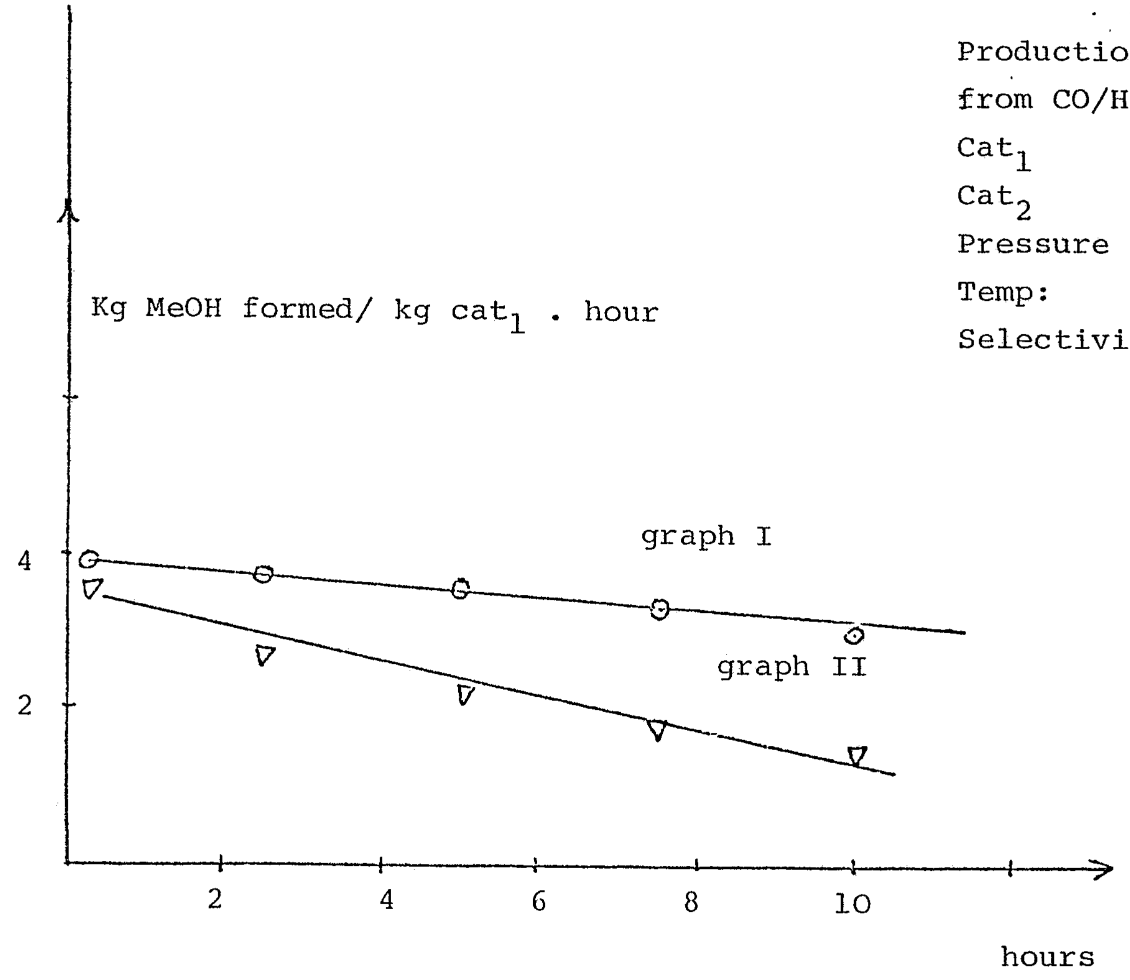


Figure 7

Production of methanol and methyl formate from CO/H_2 = 1/2 .

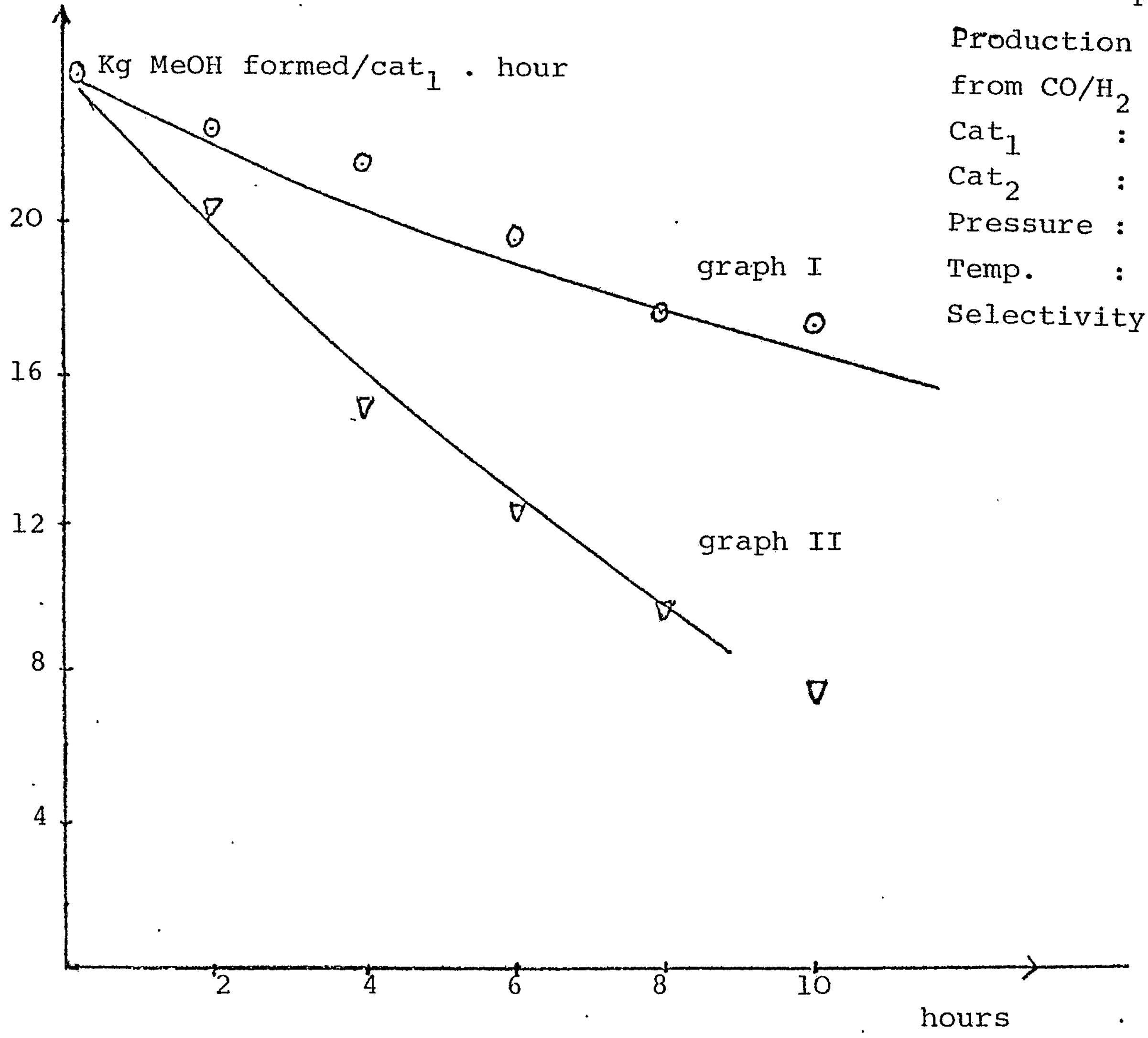
Cat$_1$: Na(OMe), 1.0 mole% in MeOH

Cat$_2$: "G89", 3.0 g

Pressure : 67 bar

Temp. : 150°C

Selectivity as regards MeOH : 89.2%



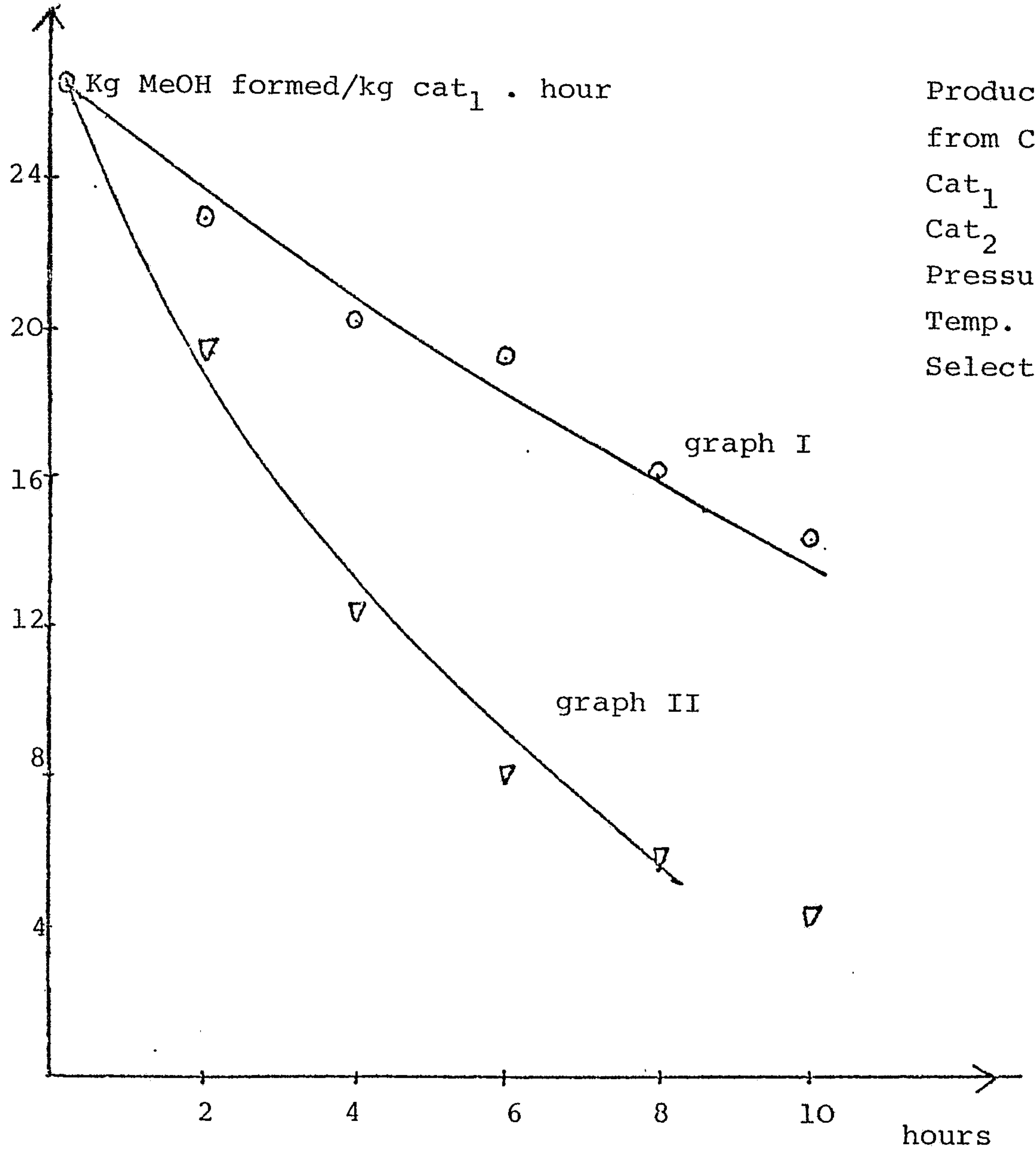


Figure 8

Production of methanol and methyl formate
from $CO/H_2 = 1/2$
Cat_1 : Na(OMe), 1.0 mole% in MeOH
Cat_2 : "G89", 3.0 g
Pressure 58 bar
Temp. : 170°C
Selectivity as regards MeOH: 92.6%

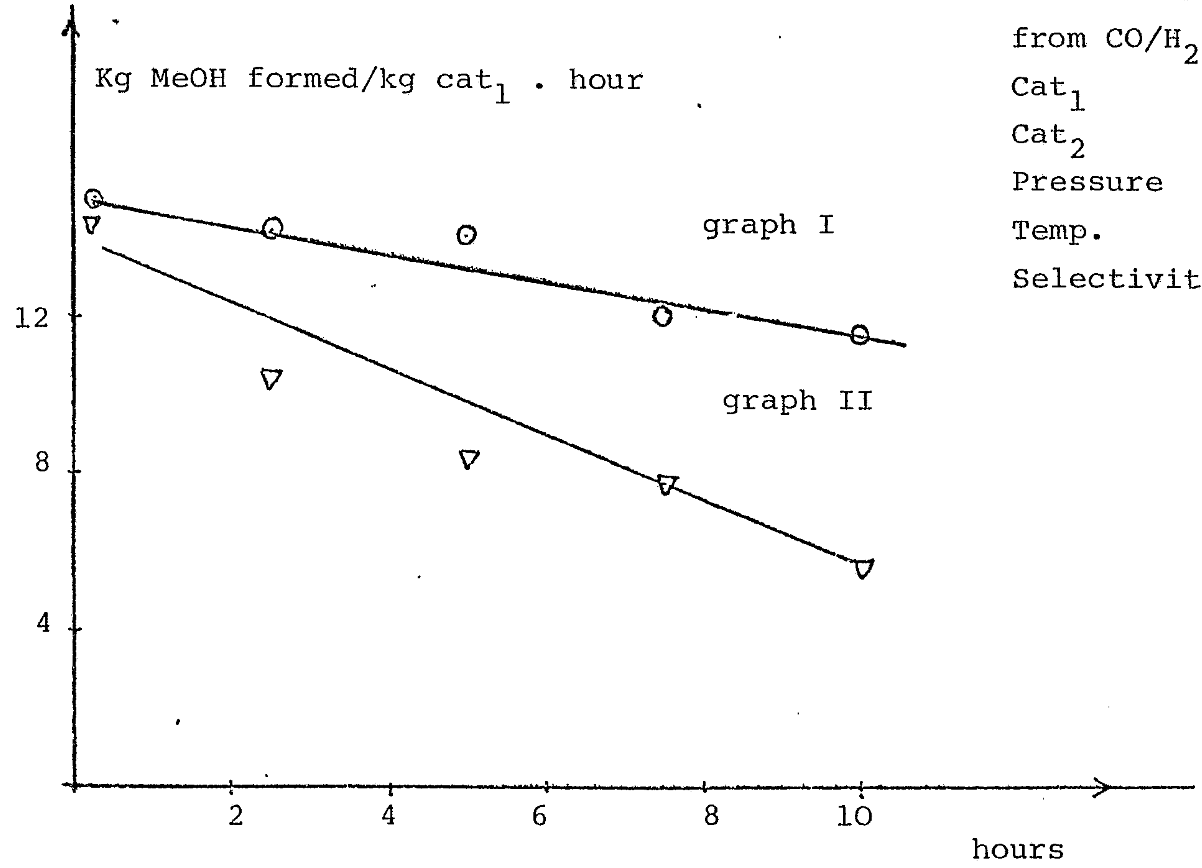


Figure 9

Production of methanol and methyl formate from $CO/H_2 = 1/2$

Cat_1 : Na(OEt), 1.0 mole% in MeOH.
Cat_2 : "G89", 3.0 g
Pressure : 75 bar
Temp. : 130°C
Selectivity as regards MeOH: 90.4 %

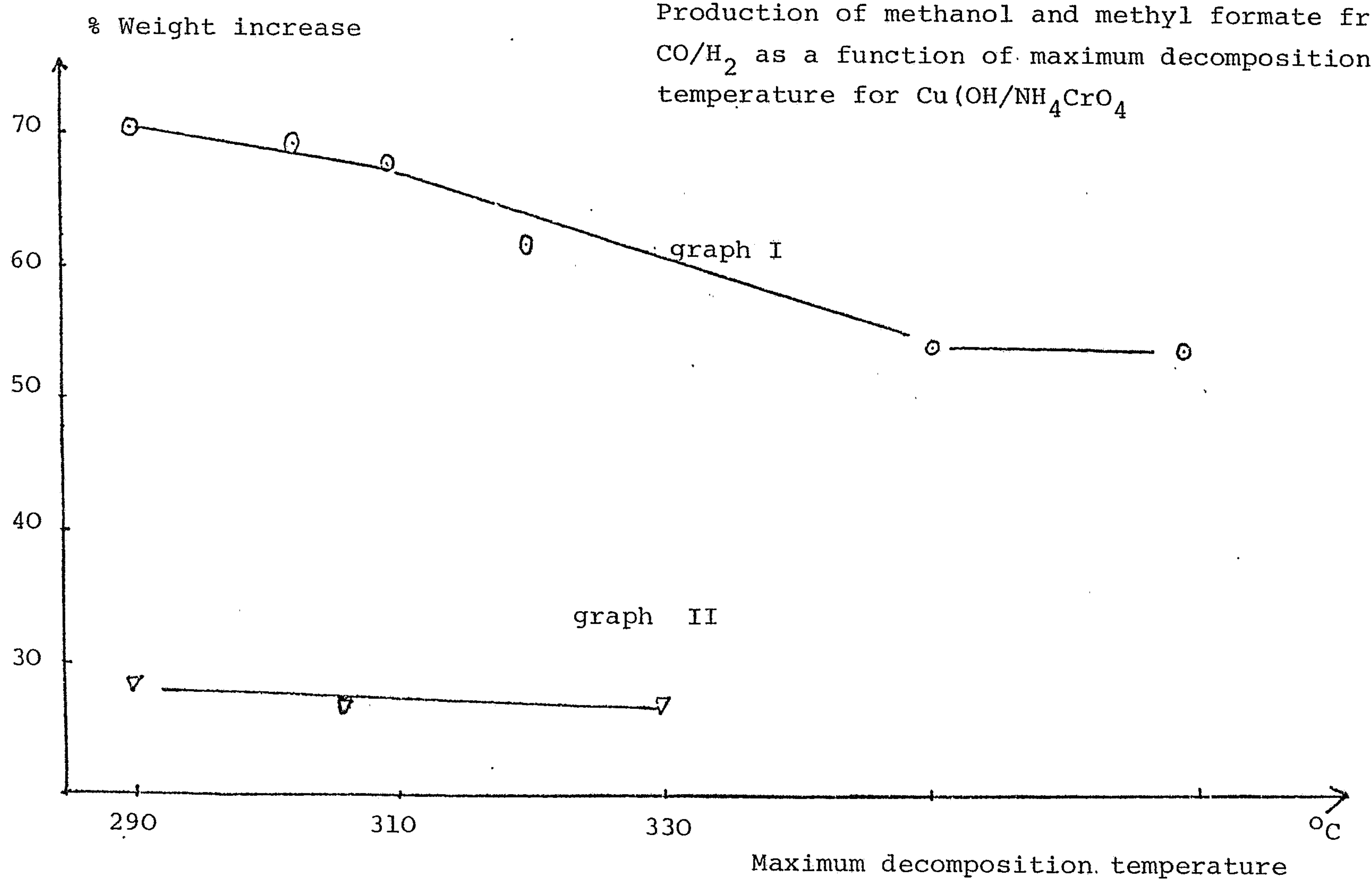
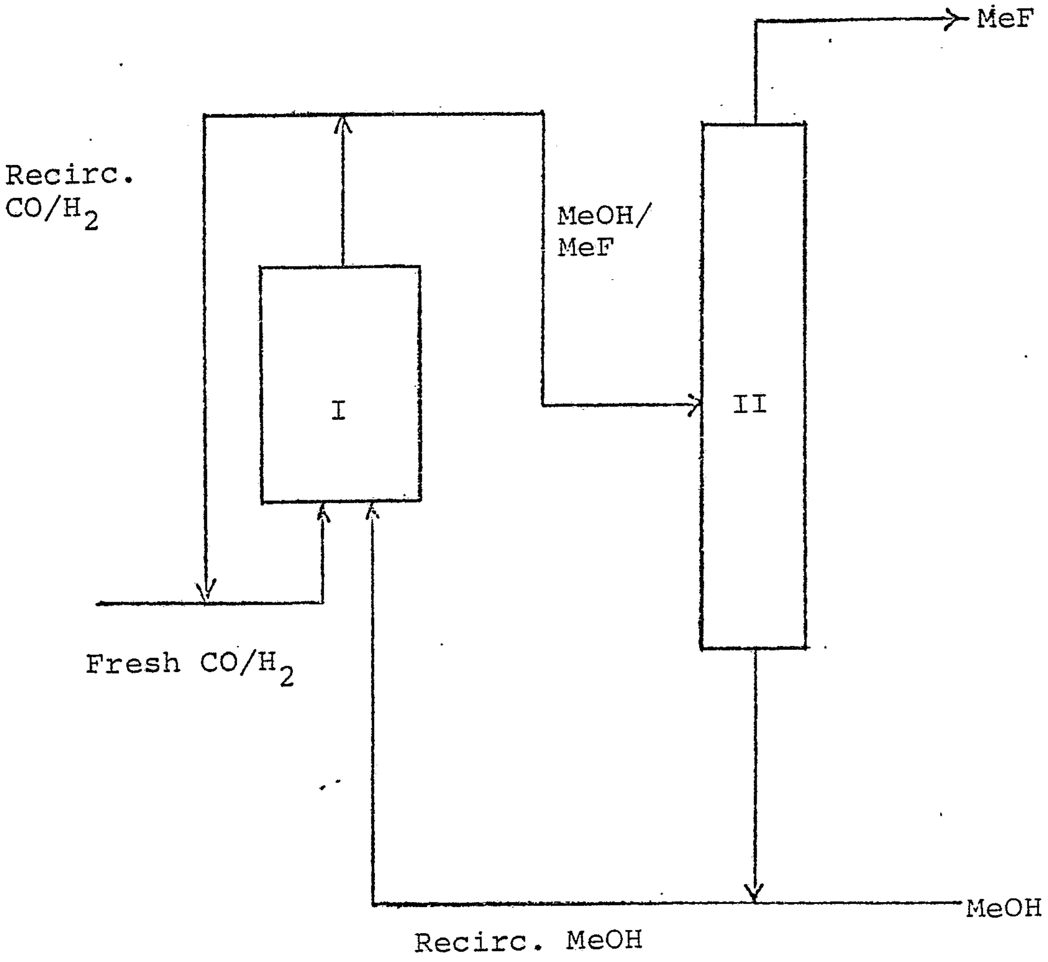


Figure 10

Production of methanol and methyl formate from CO/H_2 as a function of maximum decomposition temperature for $Cu(OH/NH_4CrO_4$

Figure 11



I) Reactor
II) Distillation unit

INTERNATIONAL SEARCH REPORT

International Application No PCT/NO82/00040

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC 3

C 07 C 27/06, 31/04, 69/06//B 01 J 23/86

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
IPC 3	C 07 C 27/00,06,08, C 07 C 29/132,136,15,16,31/04, C 07 C 69/04,06, B 01 J 23/85,86
National Cl	12o:5/01 .../...

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

SE, NO, DK, FI classes as above

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
X	DE, C, 809 803 (DEUTSCHE GOLD- UND SILBER-SCHEIDEANSTALT VORMALS ROESSLER) 2 August 1951	1-4
X	SE, C, 138 565 (DEUTSCHE GOLD- UND SILBER-SCHEIDEANSTALT VORMALS ROESSLER) 30 December 1952	1-4
X	DE, C, 860 048 (DEUTSCHE GOLD- UND SILBER-SCHEIDEANSTALT VORMALS ROESSLER) 18 December 1952	1-4
X	DE, C, 902 375 (DEUTSCHE GOLD- UND SILBER-SCHEIDEANSTALT VORMALS ROESSLER) 21 January 1954	1-4
X	GB, A, 668 342 (DEUTSCHE GOLD- UND SILBER-SCHEIDEANSTALT VORMALS ROESSLER) 12 March 1952	1-4
X	DE, B, 2 531 131 (UNION CARBIDE CORP) 22 January 1976	1-4
	.../...	

* Special categories of cited documents: [15]

"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

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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

"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

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2] 1983-02-04	Date of Mailing of this International Search Report [2] 1983 -02- 17
International Searching Authority [1] Swedish Patent Office	Signature of Authorized Officer [10] Gunilla Claesson Gunilla Claesson

International Application No. PCT/N082/00040

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

II Fields Searched (cont)

US Cl 260:468

252:467

260:449,5

V.☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE [10]

This International search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1.☐ Claim numbers ...., because they relate to subject matter [12] not required to be searched by this Authority, namely:

2.☐ Claim numbers ...., because they relate to parts of the International application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out [13], specifically:

VI.☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING [11]

This International Searching Authority found multiple inventions in this International application as follows:

1.☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the International application.

2.☐ As only some of the required additional search fees were timely paid by the applicant, this International search report covers only those claims of the International application for which fees were paid, specifically claims:

3.☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4.☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.

International Application No. PCT/N082/00040

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, 16 with indication, where appropriate, of the relevant passages 17	Relevant to Claim No 18
X	Journal of the American Chemical Society, 101:24, 1979, JS BRADLEY, "Homogeneous Carbon Monoxide Hydrogenation to Methanol Catalyzed by Soluble Ruthenium Complexes", pages 7419-7421.	1-2
X	NO, C, 30 784 (JENS ANTON CHRISTIANSEN) 7 June 1920	1-2
X	Patent Abstracts of Japan, abstract of JP 56-169634, publ. 1981-12-26.	1-2

Form PCT/ISA/210 (extra sheet) (October 1981)