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Experiments with alkaliied Zinc-Chromium - catalysts
Effect of different amounts of alkalis.

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S u m m a r y

The formation of higher alcohols using alkaliied Zinc-Chromium catalysts was investigated. Catalyst "Kul" yielded ample quantities of i-butanol. Catalyst "Stal / RB" gave some n-propanol besides i-butanol. Catalyst "Stal / Kac" produced principally substances boiling above 110 deg. C.

1) General observations and remarks

In carrying out the synthesis of methanol it is desirable to maintain constant and relatively low temperatures as far as possible over the entire extent of the catalyst (so for instance the "optimum temperature" resulting from the isothermes) or to lower at least at the end the temperature so that only in the midst a "peak" is formed. In producing higher alcohols as by-products on alkalinized catalysts on the contrary it is desired to apply higher temperatures. Therefore care must be taken in the first case (in methanol synthesis) to lead off the reaction's heat by appropriate means (single or double pipes within the catalyst, or by placing the catalyst within pipes) and to lead it to gas having a lower temperature so that this cool gas is warmed up completely to the temperature of the entrance layer of the catalyst. In the second case the reaction's heat is left in the gas whereby the temperature rises from the point of entrance to the point of exit, in some type of exponential curve. Thus in this case means for transferring the heat of reaction from the catalyst to the entering fresh gases are omitted; a simple cylindrical reaction's chamber ("Woltraum-Ofen") can be used herein. It has been

proved in the first report (2286/0) that the effect of methanol catalysts decreases with increasing temperatures (above the optimum temperature) thus obviously the yield of such a "non-cooled" reaction's space must be less than that of a "cooled" one. But on the other hand the higher alcohols are obtained in a better yield.

Such an "increasing temperature characteristic" could comparatively easily be produced in the "V 2 A" autoclave, which was used for the experiments. I have already pointed out that as a result of no preliminary heating of the gas, the first layers of catalyst are chilled. Temperature conditions can therefore widely be varied by adequately adjusting the quantity of the filling material and the speed of the gas. Unfortunately temperature can only be measured at the end of the catalyst layer; thus the conditions cannot be exactly tested. Therefore the tests have a rather preparative character, (i.e. examination of the products). If necessary, the experiments should be repeated in an autoclave better suited for these tests - having means for regulating gas pre-heating and for measuring the temperature all over the length of the catalyst.

Because the progress of temperature within the catalyst is uncertain, an exact calculation of the space velocity is impossible; it is unknown which portion of the catalyst is too cold to be able to participate in this reaction. Moreover the gas consumption cannot be calculated as easily as in the methanol synthesis because the gas consumption increases with a higher percentage of higher alcohols produced. So for instance the theoretical gas consumption for one kg is as follows:

Methanol	2.1 m ³	NTP (standard temp.)	100%
Ethanol	2.925 "	"	139%
Propanol	3.36 "	"	160%
Butanol	3.64 "	"	173.5%

Generally however the percentage of higher alcohols is 10% at a maximum. So the error is not too important.

The space velocity has to be computed therefore by determining the methanol content from the specific gravity of the product obtained in the operation (thus disregarding the higher alcohols) and calculating the gas consumption for this quantity.

Products were tested as before for their content of free acid, combined acid, aldehyde and acetone.

Higher alcohols were determined by careful fractionation of the condensate from several experiments, by salting-out the alcohol-water mixture with NaCl and drying. Three ways for drying were available:

- 1.) the azeotropic distillation wherein the higher alcohols (C₄ and higher) themselves remove the water
- 2.) an azeotropic distillation by adding benzene, carbon-tetrachloride, etc.
- 3.) drying with K₂CO₃, CaO, etc.

None of these methods was absolutely satisfactory however. A drying process with caustic lime brought great waste because the content of water of the azeotropic mixtures is relatively high. The boiling points of the pure substances being here in question and of the azeotropic mixtures will be reported later.

2) Experiments with a catalyst, containing potassium bichromate ("Kal")

Preparation of the Catalyst:

326 g Zinc Oxide (same brand as before)
73.5 g potassium bichromate

Both substances were mixed to a stiff paste by adding some water, the paste was dried, pulverized and shaped in a press (6 mm diameter).
Result of the analysis:

19.9 %	CrO ₃
76.1 %	ZnO
2.3 %	K ₂ O
<u>98.3 %</u>	(Balance moisture)

Results of a series of experiments with 100 cc catalyst at 250 atm (atmospheres excess pressure) are reported in Table 1 and in Fir. 1;

Table 1
Kal (100 cm); 250 atm

Nr. "Kal"	Temp.	RG*	D ¹⁵ ₄	g CH ₃ OH /h/lit	g CH ₃ OH /m ³ residual gas	g CH ₃ OH /h
1	375	5525	0.8231	416	82.2	41.6
2	400	5165	0.8366	250	49.5	25
3	425	5040	0.8592	191	41.2	19.1
4	450	4880	0.8999	114	24.6	11.4

* Space velocity

Condensates of experiments 1-4 were combined and had a specific gravity of 0.8479 (81.0% CH₃OH)

Free acid.....	0.03%
Combined acid.....	0.5%
Aldehyde.....	0.1%
Acetone.....	0.8%

A distillation of 106 ml gave the following figures:

B.P.....	53 deg. C.
up to 64 deg. C.....	4.5 ml
64-66 deg. C.....	67.0 ml
over 66 deg. / loss	34.5 ml

Fraction over 66 deg. C. was salted out with NaCl and dried with K₂CO₃. 7.2 ml of an oil strongly smelling of isobutanol was obtained. The total yield of alcohols is therefore about:

4.5 + 67 + 7.2 ml = 74.5% by volume (78.7 ml)

First runnings were repeatedly mixed with water and distilled again. 0.7 ml of the oil mentioned above were obtained (0.65% by volume).

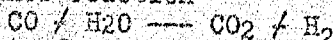
Results of the gas analyses are not reported since methane remained within the limit of 3-5%.

The quantities obtained in the single experiments were unfortunately so small that it was not possible to work them up. In a further experiment the filling material of the catalyst was still increased in order to obtain authentically a strongly ascending characteristic temperature curve. Here the alkali-free zinc chromium catalyst (already described previously) --"Stal"-- was filled in at the cold side and then only the alkali-containing catalyst "Kal", in an amount of 70 cc³ each. The results of experiments with this catalyst are reported in Table 2 and Figure 2.

Table 2
70 cm³ Stal / 70 cm³ Kal; 250 atm

Nr. "Kal"	Temp.	RG	D ₄ ¹⁵	g CH ₃ OH / h	g CH ₃ OH / n/lit	g CH ₃ OH / m ³
5	375	3900	0.8140	49.6	356	112
6	375	7500	0.8101	82.5	590	93
7	400	3330	0.8190	35.0	250	91.5
8	400	7750	0.8240	56.4	402	58.5
9	425	7500	0.8480	35.1	250	36.3

Figures interpolated for RG = 5000 are in good agreement with the Figures of Table 1 and Figure 1 (for "Kal" without addition) in the order of magnitude. Methane content remained within the limits 2.5-3.8%, while CO₂ increased, however, up to 6%. Therefore it can be assumed that a minor reaction



occurs at the cost of H₂O resulting from formation of higher alcohols.

An investigation of the combined condensates had the following results:

D ₄ ¹⁵	0.8248 (according to the Table 89.6% by wt.)
Free acid.....	0.1%
Combined acid.....	0.6%
Aldehydes.....	0.2%
Acetones.....	0.5%

In fractionating 355 ml the result was:

64-66 deg. C....	280 ml
66-74 deg. C....	3.5 ml
water / higher alc.	71.5 ml

By salting out and drying 30 ml higher alcohols were obtained (8.5% of the volume of the raw material). After adding 25 ml carbon-tetrachloride the following figures resulted:

BP. 62 deg.C.
 Up to 77 deg.C. 28 ml, 2 ml of them water
 77-88 deg.C. 1 ml
 88-104 deg.C. 0.5 ml
 104-112 deg.C. 16.5 ml (isobutyl-fraction)
 over 112 deg.C. 9.5 ml (higher than C4)

The total quantity of alcohols amounted to:

280 / 16.5 / 9.5 = 297 ml = 83.7% by vol.; isobutyl-fraction 4.6% by vol., the higher fraction 2.7% by vol.; together therefore 7.3% by vol. of the raw material.

In order to investigate more thoroughly the connection between temperature and composition of the products some experiments were carried out over a longer duration. Filling of the catalyst tube remained unchanged. Detailed description might be too long, thus only the principal data will be reported.

Experiment Kal 10

Experimental conditions: 400 deg. C. Velocity: about 1000 Lit./h measured on the gasometer after expansion ("Rota" - meter 125 mm)

Condensate: 10 1/2 hours production 890.5 ml corresponding to 85 ml in an hour average. (Minimum value: 75.5 ml; maximum value: 93.5 ml). Fluctuations show no downward trend (corresponding to decreased activity) but are connected with fluctuations in temperature and variations of the gas velocity.

Properties of the Condensate:

D₄¹⁵ 0.8215 (correspond, about 91% CH₃OH)
 Free acid 0.09%
 Combined acid 0.5%
 Aldehyde 0.2%
 Acetone 0.3%

In fractionating 830 ml the result was:

64-66 deg. C. 660 ml (?)

furthermore 78 9.4% by volume "Isobutyl oils" / 92 ml water. The 78 ml "Isobutyl oils" were worked up by adding 50 ml CCl₄. This quantity was insufficient as appeared later on. The intermediate fraction up to 100 deg. C. still disengaged some water and had to be transferred back to the flask several times after separating the water. The following figures were found:

fraction 100-112 deg. 50.5 ml (isobutyl)
 over 112 deg. 13.5 ml (higher than C4)

Total output of alcohols was:

64-66 deg.	660 ml =	79.5% by vol. (methanol)
100-112 deg. ...	50.5 ml =	6.1% by vol. (isobutanol)
over 112 deg. ..	13.5 ml =	1.6% by vol. (higher than C4)
	Total....	87.2% by vol.
Plus water ab.	100 ml....	12.1% by vol.
		99.3% by vol.
	Loss.....	0.7% by vol.

The portion containing C4 and higher was therefore 6.1 + 1.6 = 7.7% by vol. or 6.55 ml/h.

Ratio C4 to higher products is 3.8.

Experiment 11a

Experimental conditions: 425 deg. Velocity about 1500-1600 lit/h (200 mm Rotameter)

Condensate: in 5 hours 460.5 ml, corresponding to 92.1 ml/h average (minimum value 90.0 ml/h, maximum value 94.5 ml/h)

Properties:

D ₄ ¹⁵	0.8333	(corresponds to 86.5% CH ₃ OH)
Free acid.....	0.06%	
Combined acid....	0.4%	
Aldehydes.....	0.2%	
Acetones.....	0.6%	

By fractionating 450 ml the result was:

64-66 deg. C.	340 ml
66-82 deg. C.	1 ml

Furthermore: 41.5 ml "isobutyl oils" (9.2% by vol.) and about 58 ml water.

Isobutyl oils were mixed with 50 ml CCl₄, whereby still some water separated out. Result of the distillation:

B.P.	57.5 deg. C.
up to 78 deg. C.	55 ml, 3 ml of them water
78-90 deg. C.	3 ml
90-100 deg. C.	traces
100-110 deg. C.	21 ml isobutanol
over 110 deg. C.	8.5 ml (over C4)

Output of isobutanol is 4.7% by vol., of alcohols over C4: 1.9% by vol., therefore together 6.6% by vol. or 5.15 ml/h.

Ratio C4: higher products (than C4) is 2.5.

Experiment Kal 12

Experimental conditions: 450 deg., Velocity about 1900-2100 lit/h.
(Rota 260mm)

Condensate: In 5 hours 404.5 ml corresponding to 80.9 ml/h average.
(Minimum value 75 ml, maximum value 90.5 ml)

Properties:

D ₄ ¹⁵	0.8522 (corresponding to 79.3% CH ₃ OH)
Free acid.....	0.1%
Combined acid.....	0.5%
Aldehyde.....	0.2%
Acetone.....	0.9%

The result of fractionating 400 ml was:

64-66 deg. C. 281.5 ml

furthermore 38.5 ml isobutyl oils (9.6% by vol.) and about 71 ml water.

Isobutyl oils were mixed with 50 ml CCl₄ and fractionated.

B.P. 57 deg. C.

up to 78 deg. C. 56 ml, 3 ml of them water

78-82 deg. C. 4.5 ml (?)

82-100 deg. C. 3 ml (?)

100-110 deg. C. 17.5 ml (isobutanol)

over 110 deg. C. 10 ml (higher than C₄)

Output on isobutanol is 4.4% by vol., on alcohols over C₄ 2.5% by vol., together therefore 6.9% by vol. or 5.58 ml/h. Ratio C₄ to "higher than C₄": 1.76.

These experiments are represented in Figure 3 and show unequivocally that at increased temperatures the amount of fractions over C₄ increases relatively to the fractions of C₄. That is not desirable. In opposition to the opinion generally found in literature references it is suggested to work also in these cases at a not too high temperature.

Under the same conditions as in Exp. Kal 11 an experiment of longer duration - 2 days - was carried out. The following result was obtained:

Spec. Gravity.....	0.8330
Free acid.....	0.04%
Combined acid.....	0.4%
Aldehydes.....	0.3%
Acetone.....	0.1%

4250 ml = 3540 g of the raw material were subjected to distillation.

Boiling started already below 30 deg. C.: In the beginning heavy vapors developed which could not be condensed (methylated ether?)

Up to 64 deg. C. 50 ml (D₄¹⁵ = 0.787) followed. This first running

smelled aldehyde-like. An aldehyde-content of about 1.6% by vol. (calculated as acetaldehyde) was determined by the hydroxylamine reaction. By diluting with water and distilling (boiling point at the start: 31 deg.C.) and by several times repeating this operation altogether 5.7 ml "oils" were separated. Furthermore now 35 ml distilled over at 64-66 deg. C. (pure methanol). Loss in these operations was therefore 9.3 ml.

The main fraction 64-66 deg. C., to which the quantities obtained in repeated distillations of the last runnings amounted to 3173 ml = 74.6% by vol. By adding to this sum the quantity obtained from the first runnings the total output was 3206.5 ml = 75.5% by vol. thus exactly the same as in Exp. 11a.

Remaining intermediate fractions were:

61-70 deg.C.....	1 ml	
70-74 deg.C.....	28.5 ml	(D=0.8155)
74-79 deg.C.....	8 ml	
80-84 deg.C.....	12.5 ml	(D=0.8460) (Isopropyl water azeotrope ?)
Total	50.0 ml	(about 1% by vol.) (denoted as "intermediate fraction")

407 ml "isobutyl oils" and 350 ml water remained as residue.

All together 4075 ml were recovered. The relatively big loss of 175 ml = 4.1% by vol. can partly be explained by the non-condensed portions, and partly simply by the fact that the Raschig - rings of the distilling column apparatus were first dried out while they remained at the end of the operation a certain amount of liquid.

358.5 ml of the Isobutyl oils were distilled without adding any other substance by using the isobutanol itself for the purpose of azeotropic dehydration with the following result:

B.P.....	74 deg. C.	Probable Content
74-79 deg.....	0 ml	
79-84 deg.....	1 ml	(Isopropanol-water azeotrope and isopropanol)
84-88 deg.....	35 ml	(n-propanol-water azeotrope and propyl ?)
88-102 deg.....	24.5 ml	(isobutanol-water azeotrope)
further.....	3.0 ml water	

Residue (C₃ and higher): 285 ml (D₄¹⁵ = 0.8138)

This would correspond to 324 ml = 7.6% by vol. C₃ and higher when calculated on the whole amount. C₄ (isobutanol) was not separated here because the major part of the resulting product was obtained in this form.

In working up the fraction 64-66 deg. additional small quantities of oil settled out. Altogether about 31 ml = 0.7% by vol. of raw methanol were obtained; 21 ml of them were fractionated.

Boiling started at 51.2 deg.

2 ml....	56.0 deg. C.	12 ml....	68.8 deg. C.
4 ml....	58.2	14 ml....	76.0
6 ml....	59.5	16 ml....	81.6
8 ml....	63.0	18 ml....	99.5
10 ml....	67.0	19 ml....	102.0

The residue over 102 deg. had a hydrocarbon-like smell. The density of the product was determined on another sample (collected from different experiments) with 0.7747.

The combined fractions up to 102 deg. C. (D = 0.8258) contained aldehydes. After removing them by a bisulfite-treatment a mixture resulted smelling from hydrocarbons the same.

Regarding the presence of C-3-alcohols (n-propanol and isopropanol) there is a possibility that fraction 80-84 deg. (12.5 ml = 0.3% by vol.) of the intermediate fractions might contain the azeotropic mixture isopropanol-water (80.4) respect. isopropanol (82.4 deg.). The fraction obtained by distilling isobutyl oils boiling at 84-88 deg. (35 ml = 0.8% by vol.) might contain the azeotropic mixture n-propanol-water (87.7 deg.); it smelled, however, definitely like isobutanol, although the azeotropic mixture of this alcohol with water is known to boil only at 89.8 deg. But ethanol is only perceptible in traces (very slightly positive iodoform test).

It would be desirable to start experiments, giving a greater quantity of material.

3) Experiments with a catalyst, containing potassium ferricyanide (Stal / RB)

The catalyst which differed from catalyst "Stal" by addition of $K_3Fe(CN)_6$ only was prepared:

326 g ZnO
76 g Cr₂O₃
62.5g CrO₃
30 g $K_3Fe(CN)_6$

Results are reported in Table-3.

Table 3
100 ccm Stal / RB; 250 atm

Exp.Nr. Stal / RB	Temp.	RG	D ₁₅ /h	g CH ₃ OH /h	g CH ₃ OH /h/lit	g CH ₃ OH/m ³
1	375	5770	0.8568	36.2	362	72.2
2	375	9910	0.8434	29.0	290	31.2
3	400	10300	0.8610	32.7	327	34
4	425	8980	0.8788	30.0	300	36
5	425	14410	0.8550	36.1	361	26.5

The products obtained were worked up with those of Exp. 6 in the first layer of 70 cc Stal and adjoining a 70 ccm Stal / RB were used.

In six hours during test at 425 deg., gas velocity about 1500 lit/h (Rota 180-200 mm) a quantity of 309.5 ml condensate altogether was obtained; this averages 51.6 ml/h.

Properties of the condensate:

Density..... 0.8601
Free acid..... 0.1%
Combined acid... 0.7%
Aldehyde..... 0.3%
Acetone..... 0.6%

In fractionating 514 ml, resulting from experiments 1-6, the following quantities were obtained:

64-66 deg..... 329 ml
66-70 deg..... 2.5 ml
70-80 deg..... 11.5 ml
60.0 ml oil
Residue 90.0 water
 493.0 ml
(Loss 21.0 ml)

The oils were first distilled without drying them and without adding CCl_4 . In this case, however, a great quantity of a fraction 77-88 deg. C. was obtained (38 ml, having a $D_{20}^{20} = 0.8702$), which obviously contained the azeotropic mixture n-propanol-water ($D = 0.880$). This fraction which could not be dehydrated as intended first was dried later on with K_2CO_3 and distilled again. Altogether the quantities obtained were:

up to 80 deg. C..... 4.0 ml
80-85 deg. C..... 3.2 ml (isopropanol)
85-90 deg. C..... 1.7 ml
90-95 deg. C..... 0.5 ml
95-100 deg. C..... 11.0 ml (n-propanol)
100-110 deg. C..... 9.5 ml (iso-butanol)
over 110 deg. C..... 23.0 ml
 42.9 ml

Fraction 80-85 deg. C. is probably isopropanol (0.6% by vol.) fraction 95-100 consists of n-propanol (2.1% by vol.), fraction 100-110 of isobutanol (1.85% by vol.), the remainder higher than C₄ (4.5% by vol.). Ratio C₃ / C₄ to "higher than C₄" is: $(0.6 + 2.1 + 1.85) : 4.5 = \text{approx. } 1$, thus rather unsatisfactory.

The experiment was repeated (Exp. 7 and Exp. 8). The condensate showed the following properties:

Density..... 0.8517
 Free acid..... 0.09%
 Combined acid... 0.6%
 Aldehydes..... 0.3%
 Acetone..... 0.4%

Fractionate distillation of 1160 ml gave the following results:

up to 64 deg. C.... 24.5 ml
 64-66 deg. C..... 771.0 ml

Furthermore after salting-out and drying with K_2CO_3 : 88 ml "isobutyl oils" (7.6% by vol.).

By fractionating the oil (boiling started at 71 deg. C.) the following results were obtained:

	Possible Constituents
up to 79 deg. C..... 6.0 ml	ethanol-water; ethanol iodoform-test slightly positive
79-85 deg. C..... 3.0 ml	Isopropanol-water azeotr. 80.4 deg.
85-91 deg. C..... 2.0 ml	Isopropanol 82.4
91-94 deg. C.....	n-Propanol-water azeotr. 87.7
94-102 deg. C..... 15.0 ml	isobutanol-water 89.8
100-105 deg. C..... 3.0 ml	n-butanol-water 92.3
105-110 deg. C..... 10.5 ml	n-propanol 97.0
over 110 deg. C..... 43.0 ml	isobutanol 108.0
	higher than C_4

The fraction, containing isopropanol, has still decreased (0.26 % by vol.), the fraction n-propanol amounts to 1.3% by vol., the fraction isobutanol to 0.9% by vol. while the fraction "higher than C_4 " is 3.7% by vol.

The experiment should be repeated at lower temperatures. However, it has to be considered as an interesting fact that this catalyst produces by far more n-propanol than the catalyst "K₁".

4) Experiments with a potassium acetate containing zinc-chromium catalyst: (Stal / Kac)

This catalyst was prepared according to the following formula:

326 g ZnO
 76 g Cr_2O_3
 62.5 g CrO_3
 49 g acetate of potassium

(Analysis: 67.4% ZnO, 3.7% CrO_3 , 17.8% Cr_2O_3 , 3.6% H_2O , balance acetic acid / water)

Results are reported in Table 4.

Table 4
100 ccm Stal / Kac; 250 atm

Exp.Nr. Stal / Kac	Temp.	RG	D ₄ ¹⁵	g CH ₃ OH /h	g CH ₃ OH /h/lit	g CH ₃ OH/m ³
1	375	5000	0.8860	13.8	138	29.5
2	400	5220	0.8508	19.0	190	39.5
3	400	9000	0.8549	19.3	193	22.5
4	425	5335	0.8670	18.35	183.5	38.5
5	450	4060	0.8810	15.4	154	41

By comparing these values with those of the catalyst Stal / RB (from which it differs only by the use of another acid) the figures related above are throughout lower as is shown in Table 5. This table gives a comparison of the following values (for approx. RG = 5000).

Table 5
RG approx. 5000; 250 atm

g/h/lit at deg.C.	(for 100 ccm catalyst each)	
	Stal / RB	Stal / Kac
375	362	138
400	327	190
425	220	183.5
	(interpolated)	

Analysis of the combined condensates resulting from experiments 1-5 showed the following figures:

Density.....	0.8678
Free acid.....	0.4%
Combined acid...	0.3%
Aldehyde.....	0.2%
Acetone.....	0.4%

Analysis by fractionated distillation did not yield a useful result because of the small quantities of the condensate. Only 32.5 ml oil remained (from 102 ml initial material) which still contained methanol. It should be mentioned that the residue in the flask solidified to a salve-like mass. The odor was plainly different from that observed in other experiments. (Ketones ?)

Also a series of experiments using in the first layer 70 ccm Stal and 70 ccm Stal / Kac brought not very interesting results. But

also in these cases the relatively high content of combined acid remained remarkable (1.5%).

In an experiment of longer duration (N deg. 12) at 400 deg. and approx. 1000 lit/h gas velocity, where the same arrangement of catalysts as mentioned just here above was used, the production of condensate was 595.5 ml in 11 hours thus average 54 ml/hour.

Properties:

D ₄ ¹⁵	0.8323
Free acid.....	0.2%
Combined acid.....	0.9%
Aldehyde.....	0.3%
Acetone.....	0.9%

Fractionated distillation of 600 ml had the following result:

64-66 deg.....	460 ml
66-74 deg.....	2.5 ml
over 74 deg.....	54.0 ml oil
	<u>83.5 ml</u> water
	600.0 ml

These 54 ml oil were worked up together with 16 ml coming from the experiment mentioned above (translator's note: not specified, probably the 32.5 ml oil mentioned in the lower part of the previous page). After drying with K₂CO₃, 58.0 ml remained. Fractionation gave the following figures:

72-82 deg.....	1.3 ml
82-88 deg.....	3.5 ml
88-104 deg.....	3.0 ml
104-112 deg.....	13.0 ml (isobutanol)
112-150 deg.....	4.0 ml
over 150 deg.....	32.7 ml (partially solidifying)

The ratio of "higher than C₄" (32.7 / 4 = 8.175 ml) to C₄ (13 ml) is very unfavorable despite the relatively low temperature. Thus this catalyst is not very interesting.

In working with these three catalysts the CH₄-formation was so unimportant in all the experiments that the content on CH₄ rose only occasionally over 3% in spite of the working method by circulation (in cycles).

According to different references a gas mixture in the ratio CO : H₂ = 1:1 is said to be essential for forming higher alcohols, whereby half of the quantity of CO is converted into CO₂ using the water formed in the reaction. Regarding the relatively small percentage of higher alcohols - approximately 10% by vol. - obtained in these experiments formation of CO₂ did not occur and there was no difficulty in working with the usual gas mixture: one CO : two H₂.

(signature)