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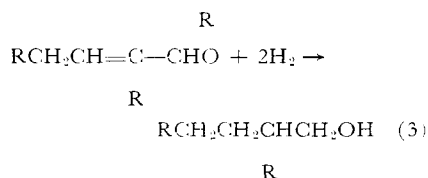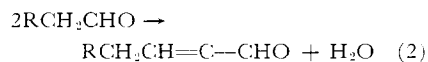Research and Engineering Division, Monsanto Chemical Co., Dayton, Ohio

# Producing 2-Ethylhexanol

## . . . by the Guerbet Reaction

### Tripotassium phosphate is the most effective condensing agent

THE ALKALINE CONDENSATION between two molecules of an alcohol to form an alcohol with an increased number of carbon atoms is known as the Guerbet reaction (6). The reaction may be represented by the general equations:

$$RCH_2CH_2OH \rightarrow RCH_2CHO + H_2 \quad (1)$$

$$2RCH_2CHO \rightarrow$$
$$RCH_2CH=C—CHO + H_2O \quad (2)$$
$$\qquad\qquad\quad R$$

$$RCH_2CH=C—CHO + 2H_2 \rightarrow$$
$$\qquad\quad R$$
$$\qquad\qquad RCH_2CH_2CHCH_2OH \quad (3)$$
$$\qquad\qquad\qquad\qquad R$$

This condensation reaction is applicable only to those primary and secondary alcohols which contain a methylene group adjacent to the carbon atom containing the hydroxyl group. Isobutyl and cinnamyl alcohols, which do not possess the requisite structure, do not self-condense to form the expected dimolecular alcohols (24).

*Simultaneously with higher alcohol formation, the acids which are formed, often in equimolar amounts, constitute a serious disadvantage to the use of the Guerbet reaction (2, 4, 7, 16, 21).* This report describes the results of an extensive study on the Guerbet reaction with particular emphasis on the selection of an alkaline reagent which would allow maximum reproducible conversions of n-butyl alcohol to 2-ethylhexanol under practical reaction conditions while minimizing acid formation.

## Experimental

**Apparatus.** The majority of the Guerbet condensations were carried out in an Aminco bottom-stirred autoclave, fabricated from Type 316 stainless steel. This autoclave had an approximate volume of 1410 ml., with an operating pressure of 4500 p.s.i. at 300° C. It was originally equipped with propeller-type agitation, mounted inside the vessel on a rotating shaft and driven at 450 r.p.m. by a 1½-hp. variable speed motor.

The head of the clave was originally fitted with a baffle, an internal high pres-sure cooling coil (water), and a valve-controlled dip tube. These parts subsequently failed from caustic embrittlement and were removed. A thermocouple well was also mounted on the autoclave head.

Later modifications, necessitated by efforts to remove water azeotropically from the reaction, included a 3-foot fractionation column mounted above the autoclave. The column was fabricated from Monel and had an inside diameter of ¼ inch. The column was fitted with a Monel screen at the lower end and packed with about 0.25 liter of 0.16 × 0.16 inch nickel cannon packing. The column was electrically heated and wrapped. The top and several points along the length of the column contained hypodermic-type thermocouple wells, which were connected to a temperature recorder.

A 3-foot tube condenser of 9/16-inch pressure tubing welded inside a steel pipe was mounted at the upper end of the fractionation column. The steel pipe served as a jacket for circulating cooling water.

A water trap, interposed between the condenser and column, was a Type 316 stainless steel autoclave having a capacity of about 110 ml. and an outside diameter of 2 9/16 inches. This was also jacketed for water cooling.

Gas evolution from the ethyl alcohol condensations was measured by slowly bleeding the residual pressure of the cooled autoclave through two dry-ice traps connected to a gas collection tube fitted with a valved bypass and then to a wet test meter. Composition of the gases was determined with a mass spectrometer. The dry-ice trap usually contained small amounts of acetaldehyde.

All laboratory distillations were carried out in a Todd precise fractionation assembly, fitted with a column 12 mm. in diameter and packed with 3/32-inch diameter borosilicate glass helices.

**Procedure.** In a typical experiment, 544.0 grams of n-butyl alcohol, 53.0 grams of tripotassium phosphate, 84.0 grams of calcium oxide, and 20.0 grams of activated copper were placed in the autoclave. The clave was sealed and pressure tested for leaks with 1000 p.s.i. of nitrogen. When the clave was secure, the nitrogen pressure was slowly bled off through the vent. The vent valve was closed, the stirrer started, and heat applied. The reaction attained the desired temperature within 1 hour, and was maintained at 293° to 295° C. for 4.5 hours. The maximum pressure developed during the reaction was 2250 p.s.i. After the reaction cooled to room temperature, the residual pressure (950 p.s.i.) was vented, and the autoclave emptied. The contents were filtered, the filtrate washed with water to remove acid salts and extracted with benzene. The benzene extracts were added to the organic material and this mixture dried over magnesium sulfate.

Distillation yielded 45.5 grams of an n-butyl alcohol–water azeotrope, 185.0 grams of n-butyl alcohol, and 162.0 grams (1.24 moles) of 2-ethylhexanol, distilling at 181° to 185° C. A residue of 24.5 grams remained after distillation. The conversion to 2-ethylhexanol was 41.5% and the yield was 75.6%.

In those experiments where acid

## Through this work, several difficulties may be solved...

▶ **Acid formation is reduced and enhanced catalyst activity is shown by using tripotassium phosphate**

▶ **High boiling residues are converted to useful products**

▶ **Water of reaction is removed by azeotropic distillation**

values were determined, the aqueous washings were acidified, then extracted with ether. The ether was removed, and the liquid residue was dissolved in 20% aqueous sodium carbonate and re-extracted with ether. The ether extracts were discarded, and the aqueous solution acidified with cold hydrochloric acid. The acids were taken up in ether and dried. The solvent was removed and the acids were weighed.

**Hydrogenolysis of High Boiling Residues.** Hydrogenolysis of the residues was investigated in order to convert this material to additional useful products. A sample of these residues from the condensation of n-butyl alcohol was carefully fractionated to remove traces of 2-ethylhexanol and low boiling esters. A 1000-ml. rocking autoclave was charged with 257.6 grams of this material, 15.5 grams of copper chromite catalyst, and hydrogen at a pressure of 1600 p.s.i. When the desired temperature had been reached, the hydrogen pressure was boosted to 3600 p.s.i. The autoclave was heated and rocked at 250° C. for 5 hours. Then the bomb was cooled, the contents filtered to remove the catalyst, and the filtrate distilled. n-Butyl alcohol (5.6 grams) and 2-ethylhexanol (21.4 grams) were recovered.

The residual material, 204.0 grams, was recharged to the clave with 20.0 grams of copper chromite and hydrogen at a pressure of 3000 p.s.i. The reaction was held at 250° C. for 7 hours. An additional 6.0 grams of n-butyl alcohol and 13.0 grams of 2-ethylhexanol were obtained. The total recovery from both experiments amounted to 4.5% (based on weight of residue charged) of n-butyl alcohol and 13.3 weight per cent of 2-ethylhexanol.

Continued distillation gave 35.0 grams (13.5%) of a substance, distilling at 106° – 108° C. for 4 mm. of mercury ($n_D^{25}$, 1.4482; $d_4^{20}$, 0.840). This fraction was identified by infrared analysis as a saturated primary alcohol. This is believed to be a branched chain dodecyl alcohol. A second fraction of 17.8 grams (7%), which distilled at 133° to 140° C. for 3 mm. of mercury ($n_D^{25.5}$, 1.4668-9) was shown to be a primary alcohol by infrared analysis, possibly 2,4,6-triethyldecanol.

Analysis. Calcd. for $C_{16}H_{34}O$: C, 79.28; H, 14.10. Found: C, 79.28; H, 13.69. The hydrogenolysis of a second batch (292.4 grams) of high boilers was accomplished with 50.0 grams of copper chromite and hydrogen

## Products Identified from n-Butyl Alcohol Residues Prior to Hydrogenolysis

| Compd. | B.P., ° C. | | $n_D^{25}$ | $d_4^{25}$ |
| --- | --- | --- | --- | --- |
| | 1 Atm. | 3-Mm. Hg | | |
| 2-Butylethylhexoate | 229–230 | 77–78 | 1.5203 | 0.854 |
| 2-Ethylhexyl butyrate | 235–237 | 82–83 | 1.4236 | 0.860 |
| 2-Ethylhexyl 2-ethylhexoate | 291–293 | 118–119 | 1.4312 | 0.853 |

at a pressure of 2000 p.s.i. and 250° C. for 12 hours. Distillation gave 11.9 grams (4%) of n-butyl alcohol, 13.1 grams (4.4%) of 2-ethylhexanol, 56.5 grams (19%) of the dodecyl alcohol, and 48.5 grams (16.6%) of the hexadecyl alcohol.

Analysis of dodecyl alcohol, presumably 2,4-diethyloctanol. Calcd. for $C_{12}H_{16}O$: C, 77.45; H, 13.97. Found: C, 77.66; H, 13.46

The esters from n-butyl alcohol residues were saponified using 0.1N potassium hydroxide in diethylene glycol (19). The alcohol moieties were identified by the preparing their respective 3,5-dinitrobenzoates and/or 3-nitrophthalates. n-Butyl 3,5-dinitrobenzoate had a melting point of 63.2°–63.4° C. [62.5°–64.0° C. (3)]. 2-Ethylhexanol formed a 3,5-dinitrobenzoate, melting point 23°–23.5° C. (11), and a 3-nitrophthalate, melting point 109°–110° C. [107° C. (23)]. The preparation of a 3-nitrobenzoate or phenylurethane from 2-ethylhexanol failed (7). The dodecyl and hexadecyl alcohols failed to yield crystalline derivatives. 2-Ethylhexoic acid, isolated by saponification of these esters, formed an amide melting at 102°–103° C. [102°–103° C. (25)].

n-Hexyl alcohol and 2-ethylbutanol were isolated from the Guerbet condensations of ethyl alcohol. The 3,5-dinitrobenzoate of n-hexyl alcohol had a melting point of 58°–58.4° C. (11), but the 3,5-dinitrobenzoate of 2-ethylbutanol melted at 47.6°–47.8° C. [51.5° C. (11)]. The 3,5-dinitrobenzoate of 2-ethylbutanol formed an addition compound with α-naphthylamine, melting point 81.8° C. [82.5° C. (11, 22)].

Acetaldehyde and butyraldehyde (2,4-dinitrophenylhydrazone; melting point 122°–123° C.) were also obtained in small amounts.
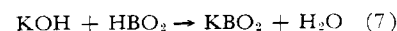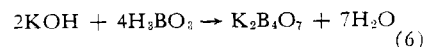
## Results and Discussion

**Alkaline Condensing Agents.** Various alkaline condensing agents show a considerable difference in effective-

ness. Potassium cyanide, piperidine acetate, and sodium methylate were totally ineffective. Sodium methylate, in fact, appeared to decompose during the reaction. The conversions of 2-ethylhexanol were low (10 to 15%) from either n-butyl alcohol or ethyl alcohol using sodium acetate, sodium or potassium butyrate (18), or nonreducible metallic oxides, often promoted with cobalt or chromium salts (8, 9), as condensing agents.

Alkali metal carbonates were also studied as condensing agents for the Guerbet reaction. Ethyl alcohol was converted to a mixture of alcohols, including n-butyl alcohol (5 to 10%), hexyl alcohols (2 to 6%), and octyl alcohols (2 to 7%) in 8 hours at 250° C. The condensation of n-butyl alcohol by means of potassium carbonate gave 10 to 12% conversion to 2-ethylhexanol. These results (Figure 1) parallel those previously reported (5).

A mixture of potassium hydroxide and boric anhydride is reported (21) to give good yields of 2-ethylhexanol while minimizing oxidation of alcohol to carboxylic acids. Although a 33.5% conversion of n-butyl alcohol to 2-ethylhexanol was obtained at 290° C. after 10 hours, a poor reproducibility of results was obtained in carefully replicated reactions. Acids and high-boiling residues were also formed in substantial amounts. Similar observations have been recorded previously (7).

The relationships involved in the system KOH/$B_2O_3$, especially in the presence of water and at the temperatures employed for the Guerbet reaction, are complex. Boric anhydride is successively hydrated to m- and o-boric acids, the former reaction being much faster than the succeeding one (13). o-Boric acid ($H_3BO_3$), however, is known to dehydrate to m-boric acid, ($HBO_2$), at 100° to 150° C. m-Boric acid is stable at 170° to 200° C. (15, 20). Consequently, during a Guerbet reaction utilizing the KOH/$B_2O_3$ mixture, the following reactions are possible:
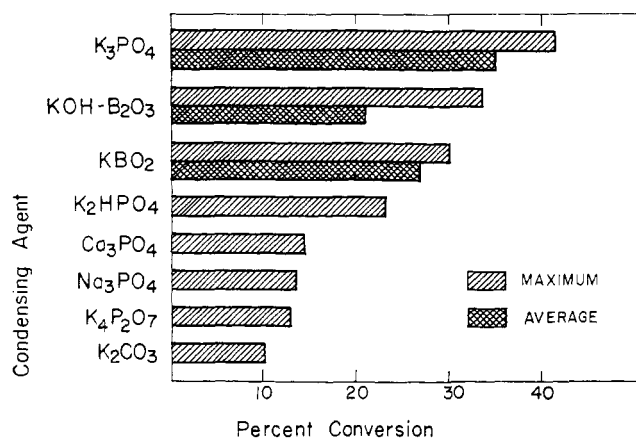
$$3B_2O_3 + 5H_2O \rightarrow 4HBO_2 + 2H_3BO_3 \quad (4)$$

$$H_3BO_3 \xrightarrow{150° C.} HBO_2 + H_2O \quad (5)$$

$$2KOH + 4H_3BO_3 \rightarrow K_2B_4O_7 + 7H_2O \quad (6)$$

$$KOH + HBO_2 \rightarrow KBO_2 + H_2O \quad (7)$$

## Current Uses

2-Ethylhexanol is used as a solvent, as a defoaming agent, and as a dispersing agent for pigments. Esters with dicarboxylic acids, such as di(2-ethylhexyl) phthalate, are excellent plasticizers for synthetic resins and rubbers. The sodium sulfate derivative of the alcohol is used as a wetting agent

Figure 1. With tripotassium phosphate reproducible conversions of 35 to 41% and yields of 77 to 83% were obtained



Figure 2. The mole ratio of tripotassium phosphate to n-butyl alcohol influences conversion

This investigation has shown that potassium tetraborate is ineffective for the Guerbet reaction. The erratic results obtained with the potassium hydroxide–boric anhydride system depend presumably on the formation rate for potassium metaborate, and on the amount of potassium tetraborate formed. Thus, formation of the actual catalyst, the potassium alcoholate, may be slow and somewhat unpredictable.

It was further shown that the use of potassium metaborate in the Guerbet condensation gave reproducible conversions (18 to 27%) of n-butyl alcohol to 2-ethylhexanol at 290° C. and 5 hours. The use of 0.5 to 1.0 mole of KBO₂ was equally effective for this conversion. This base rapidly deteriorated with repeated use because tetraborate was formed in increasing amounts.

This experimental work culminated in the selection of tripotassium phosphate as the preferred condensation reagent for the Guerbet reaction (14) (Figure 1). The conversions of n-
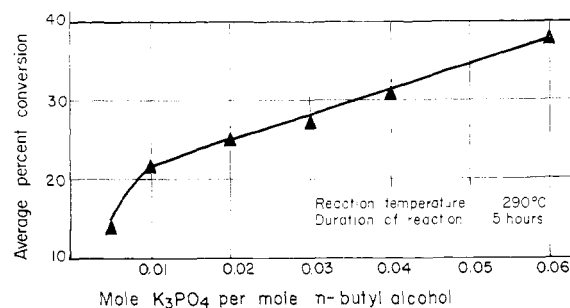
butyl alcohol to 2-ethylhexanol at 290° C. and 5 hours reaction time, and a tripotassium phosphate concentration of 0.04 mole per mole of n-butyl alcohol, were 29 to 41%. The enhanced activity of this compound was further demonstrated in the 18 to 36% conversions of 2-ethylhexanol obtained with 0.01 to 0.02 mole concentrations of the phosphate (Tables I and II) (Figure 2).

A definite order of efficiency existed among different alkaline reacting phosphate compounds. Tripotassium phosphate is more effective as a Guerbet reagent than dipotassium hydrogen phosphate, which is more active than tetrapotassium phosphate. Potassium tripolyphosphate was inactive. These results may be attributed to the differences in the ionization constants of the respective bases.

The effectiveness of alkali metal or alkaline earth phosphate is directly related to the electropositivity of the metal atom. Tripotassium phosphate is more effective for Guerbet condensations than the trisodium salt. Tricalcium phosphate, although less active than the potassium salt, appears to be the most active calcium salt for this condensation. Previous investigators have noted that potassium metal and hydroxide are more active than sodium and sodium hydroxide (16, 24). Among salts of butyric acid, the order of activity has been indicated as rubidium, potassium, and sodium (18). Calcium and cal-

Table I. Alkaline Phosphates Are Effective For Converting n-Butyl Alcohol[a] to 2-Ethylhexanol

(290° C. for 5 hours)

| Phosphate | Condensing Agent | | 2-Ethylhexanol | | Residue,[c] |
|---|---|---|---|---|---|
| | Moles | CaO,[b] moles | % conv. | % yield | % Yield |
| K₃PO₄ | 0.25 | 1.0 | 40.0 | 81.6 | 13.6 |
| | 0.37 | 0.5 | 38.4 | 88.8 | 13.8 |
| | 0.25 | 1.5 | 41.5 | 86.5 | 13.5 |
| | 0.12 | 1.0 | 36.0 | 90.7 | ... |
| | 0.06 | 0.25 | 18.0 | 80.4 | 18.3 |
| | 0.06 | 0.12 | 26.9 | 64.6 | 14.8 |
| K₂HPO₄ | 0.25 | 0.5 | 23.6 | 78.0 | 15.0 |
| K₄P₂O₇ | 0.25 | 0.5 | 12.8 | 75.5 | 14.8 |
| Na₃PO₄ | 0.12 | 0.5 | 14.7 | 78.0 | 18.5 |
| Ca₃(PO₄)₂ | 0.25 | 0.5 | 15.4 | 85.5 | 16.4 |

[a] 6.0 moles of n-butyl alcohol and 4.5 wt. % of activated copper powder. [b] Used to remove the water of reaction. [c] Calculated as C₁₂H₂₃OH.

Table II. Excellent Conversions Were Obtained, Using K₃PO₄ and Azeotropic Removal of Water at 600 to 650 P.S.I.

| C₄H₉OH, Moles | Condensing Agent | | Time, Hr. | Temp., ° C. | | H₂O Removed, Moles | 2-Ethylhexanol | | | Acid[a] Mole Ratio/ C₈H₁₇OH |
|---|---|---|---|---|---|---|---|---|---|---|
| | K₃PO₄, moles | Ni, g. | | Pot | Column | | Moles | Conv. % | Yield % | |
| 13.5[b] | 0 | ... | 1.0 | 270–282 | 184–206 | 4.3 | ... | ... | ... | ... |
| 9.9 | 0.25 | 4.0 | 5.25 | 272–288 | 200–232 | 2.0 | 3.0 | 41.3 | 79.2 | 1:26.0 |
| 12.1[c] | 0.25 | 4.0 | 4.5 | 282–286 | 218–228 | 1.6 | 1.6 | 27.4 | 83.0 | 1:13.0 |
| 12.2 | 0.25 | 4.0 | 5.5 | 275–285 | 221–228 | [d] | 1.0 | 16.2 | 57.8 | ... |
| 11.7 | 0.37 | 10.0[e] | 5.5 | 288–292 | 195–215 | 2.0 | 1.25 | 34.8 | 72.8 | 1:20.5 |
| 10.7 | 0.37 | 10.0[e] | 5.5 | 290–295 | 169–180 | 3.97 | 2.52 | 41.4 | 77.0 | 1:18.0 |

[a] Calculated as n-butyric acid. [b] This experiment served as a model; 4.5 moles of water were charged. [c] Also contained 0.19 moles of 2-ethyl-2-hexenal. [d] No water removal was attempted during this reaction. [e] 1:1 Ni-CuCrO₂.

cium hydroxide are almost totally ineffective as Guerbet condensing agents (25).

**Effect of Removal of the Water of Reaction.** The water of reaction must be removed as rapidly as it is formed in order to supress oxidation of the alcohols to carboxylic acids. Azeotropic distillation (16), and calcium or magnesium oxides (5), have been employed for this purpose. The water split out during the reaction does not participate further in the reaction, as in the addition to the double bond of the crotonized intermediate [Equation 2 (10)]. The presence of 10 to 25 weight per cent of water in the n-butyl alcohol does not impede the reaction; however, acid formation is proportionately increased (Table II).

In this investigation, both methods of removing water were employed. Azeotropic distillation of the water of reaction is superior to the use of calcium oxide in that a higher yield to charge ratio is obtained. The azeotropic removal of water from a 70 to 30 n-butyl alcohol–water mixture was demonstrated at 650 p.s.i. This represented the autogenous pressure of n-butyl alcohol–water at 270° to 282° C.; presumably other gaseous products were absent because neither alkali nor dehydrogenation catalyst was charged. When the Guerbet reaction was attempted, further pressure developed, principally from hydrogen formation. Water could not be azeotroped at 1000, 800, or 700 p.s.i. from these n-butyl alcohol condensations. The pressure was therefore regulated at 600 p.s.i. and azeotropic distillation was possible. The conversions of n-butyl alcohol to 2-ethylhexanol were 34 to 41% (Table II). These results are equivalent to the optimum results obtained using calcium oxide as a dehydrating agent (Table II). The mole ratio of acid to dimer alcohol was decreased from 1 : 2 to 9 to 1 : 13 to 26 (Figure 3).

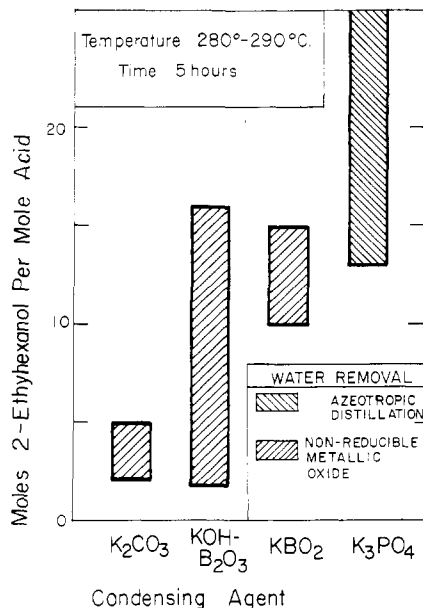**Effect of Dehydrogenation Catalysts.** The Guerbet condensation has been



Figure 3. For removing the water of reaction, azeotropic distillation is superior to metallic oxides

improved somewhat by the use of catalytically active metals in conjunction with the basic reagent. The metallic catalyst facilitates dehydrogenation of the reactant alcohol [Equation 1 (10)], and saturation of the crotonized intermediate by hydrogen interchange [Equation 3 (16)]. Saturation of such crotonized compounds by hydrogen in the presence of hot alcoholate solutions is a slow reaction in the absence of catalytically active metals (12).

Dehydrogenation catalysts have been employed in amounts of 1 to 9% of the alcohol charged. Raney nickel produced the largest amount of gaseous by-products (5), the average volume being 6 to 7 liters per mole of ethyl alcohol. Activated copper catalysts generally gave less than 4 liters per mole. The addition of promoters, such as cobalt oxalate, to the activated copper catalysts increased the volume of gaseous products to 5.5 to 5.9 liters per

mole of alcohol. Carbon-carbon cleavage and gaseous by-product formation (2.3 to 3.7 liters per mole of ethyl alcohol or n-butyl alcohol) were most effectively minimized by the use of copper chromite as the dehydrogenation catalyst. In contrast to a previous report (16), carbon-carbon cleavage was observed in all experiments (Table III). Moreover, both carbon-carbon cleavage, and the volume of off-gases, appeared to increase with increased reaction temperature.

Adding aldehyde (1, 16), such as crotonaldehyde, 2-ethyl-2-hexenal, and butyraldehyde, did not increase the 2-ethylhexanol conversion significantly (Table II). Dimethyl butyral was also without beneficial effect on the course of the reaction.

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Table III. Composition of the Off-Gases Indicates Carbon-Carbon Cleavage during Conversion of Ethyl Alcohol to Higher Alcohols

| Temp., ° C. | Dehydrogenation Catalyst | Off-Gases[a] | | | | | |
| | | Liters | Liters/ Mole $C_2H_5OH$ | Compn., Volume % | | | |
| | | | | $CO_2$ | CO | $CH_4$ | $H_2$ |
|---|---|---|---|---|---|---|---|
| 300 | CuCrO₄ | 37.5 | 3.3 | 2.5 | ... | 21.2 | 76.4 |
| 300 | CuCrO₄ | 39.3 | 3.5 | 1.8 | ... | 15.6 | 81.4 |
| 280 | Ni | 67.3 | 6.0 | 5.2 | ... | 52.3 | 42.5 |
| 300 | Ni | ... | ... | 2.9 | 70.8 | 19.9 | 6.6 |
| 300 | Cu-CoC₂O₄ | 83.0 | 3.8 | 6.9 | 2.7 | 9.1 | 81.1 |
| 300 | Cu-CoC₂O₄ | 22.8 | 2.0 | 2.5 | Trace | 48.5 | 48.5 |
| 352 | Cu-CoC₂O₄ | 47.9 | 4.9 | 11.7 | 30.3 | 18.9 | 39.1 |
| 380 | Cu-CoC₂O₄ | 88.8 | 9.1 | 15.9 | 16.1 | 29.8 | 38.2 |
| 300 | Cu-Ni | ... | ... | 13.7 | ... | 83.6 | 2.8 |
| 288 | Cu-Ni | 67.3 | 6.5 | 7.6 | 3.9 | 14.7 | 4.2 |

[a] Traces of unsaturated hydrocarbons were indicated in all determinations.