

THERMAL REACTIONS OF METHANOL UNDER BASIC CON-
DITIONS AND IN THE PRESENCE OF CARBON MONOX-
IDE

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Abstract. The thermal reduction and decompo-
sition of methanol was studied between 100
and 300°C under basic conditions and an
initial carbon monoxide pressure of 70 bar,
using different methanol to water ratios.

Methanol is industrially converted to
acetic acid and methyl formate by its reac-
tion with carbon monoxide (CO) in the pre-
sence of transition metal catalysts^{1,2}. The
formation of methane from methanol has also
been observed in a catalysed reaction with
pressurized CO³. Biomass and lignites can
be reduced to liquids with pressurized CO
under basic conditions without catalysts⁴⁻⁶.
We have studied the possibility of reducing
methanol with CO in the absence of a cata-
lyst under the conditions used for biomass
and lignite liquefaction.

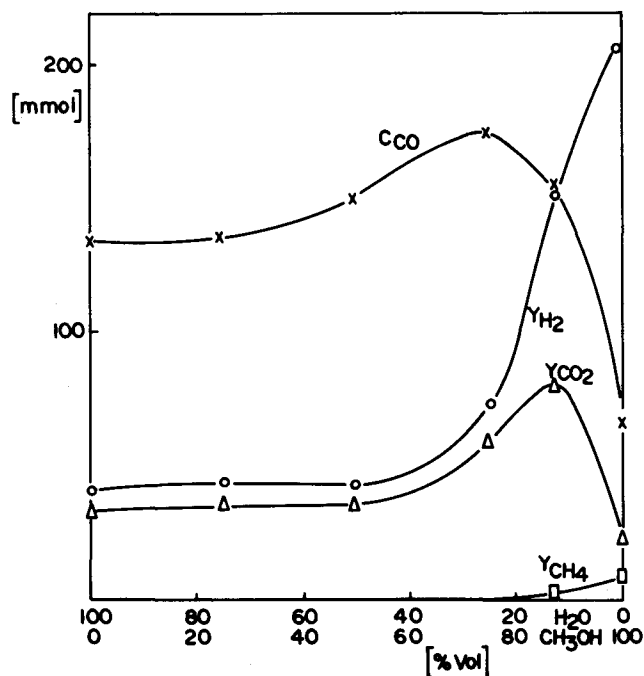
The reactions were carried out in a 200
ml autoclave⁷ containing 100 ml of methanol
or methanol-water mixture, 0,1 mol of sodium
hydroxide and 70 bar of CO (25°C). In a
first series, the liquid used was varied
from pure water to pure methanol and the
reaction system heated to 300°C during 15 min.
In a second series pure methanol was used and
the reaction temperature varied between 100
and 300°C with the same reaction time of 15
min. The reaction gases were depressurized
at 65°C and analyzed for H₂, CO, CO₂ and CH₄
using a gas chromatograph equipped with a 4,5
m Porapak Q column and a thermal conductivity
detector. From the gas analysis and the
final pressure of the reaction gases the con-
version of CO and the yields of H₂, CO₂ and
CH₄ were calculated and are given in mmol for
better comparison.

The gas yields as a function of the
methanol-water ratio are shown in Figure 1.
The CO conversion reaches a maximum at a 3:1
ratio and then decreases considerably. The

CO₂ yield also passes through a maximum at a
7:1 ratio while the H₂ yield increases rap-

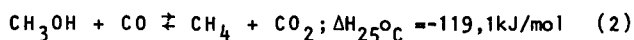
Figure 1. Conversion of CO and yields of H₂,
CO₂ and CH₄ as a function of the methanol-
water ratio.

M_{NaOH} = 1 mol/l, p_i = 70 bar CO, T = 300°C



idly for higher methanol-water ratios. The
amount of CH₄ formed is small, reaching 6,6
mmol for pure methanol. In Figure 2 the gas
yields are shown for the reaction in pure
methanol varying the temperature from 100 to
300°C. The CO conversion shows a maximum
around 230°C. The H₂ yield increases mark-
edly with temperature while the CO₂ and CH₄
yields also increase.

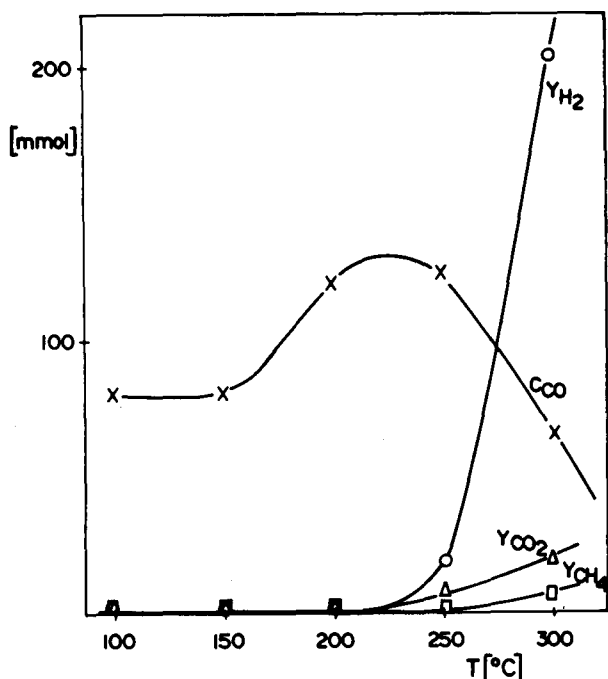
Up to a methanol-water ratio of 3:1,
about 100 mmol of sodium formate is formed,
as can be seen by the difference of the CO
conversion and the yield of H₂ which is
produced by the thermal decomposition of the
formate⁸. At higher ratios H₂ is formed by
methanol decomposition which also produces
CO (equation 1) and, therefore, reduces the
CH₃OH ⇌ 2H₂ + CO; ΔH_{25°C} = + 128,2 kJ/mol (1)
formal CO conversion. CH₄ is formed by
methanol reduction (equation 2) which is



slow under these reaction conditions. In pure methanol, up to 200°C, only sodium formate formation is observed. At 250°C the methanol begins to decompose again, reducing

Figure 2. Conversion of CO and yields of H₂, CO₂ and CH₄ from methanol as a function of temperature.

M_{NaOH} = 1 mol/l, p_i = 70 bar CO



CO conversion and accelerating H₂ formation. At 300°C methanol decomposition becomes predominant but small amounts of CH₄ are formed by methanol reduction.

For better understanding of this reaction system we calculated the reaction constants for the temperature range studied. The constant for the endothermic methanol decomposition increases from 0,1 at 100°C to 10⁴ at 300°C while the constant for the exothermic methanol reduction decreases from 10²⁰ at 100°C to 10¹² at 300°C (calculated for normal pressure).

Methanol reduction is thermodynamically highly favored between 100 and 300°C. On the other hand the amount of CH₄ formed is very small, showing that a catalyst is required in order to obtain a higher CH₄ yield. This is in agreement with the water gas shift reaction (water reduction) which is kinetically

controlled up to 400°C in the absence of a catalyst⁹. Methanol decomposition, whose reaction constant is greater than 1 above 150°C, is kinetically less hindered as can be seen by the facile H₂ production at 300°C. On the other hand, the 204 mmol H₂ formed from about 2 mol of methanol at this temperature show that equilibrium is not reached under these conditions.

Our results indicate that, under the liquefaction conditions of biomass and lignite, methanol reduction is very slow. In future studies catalysts will be used which can accelerate this reaction, preferentially at low temperatures where methanol decomposition is thermodynamically unfavorable. The influence of other variables, such as CO pressure, base concentration and reaction time will also be studied.

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