

## METHANE FORMATION DURING HYDROGENATION REACTIONS IN THE PRESENCE OF RANEY NICKEL CATALYST

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In the amination of polysubstituted acetonitrile in methanolic solution over Raney nickel under 100 bar hydrogen, an unexpected pressure build-up occurred. The only possible reason is a catalytic conversion of the solvent methanol to methane with simultaneous heating of the reaction mixture. Methane formation was proved in the laboratory, starting at a temperature as low as 110° C. It was possible to give a satisfactory description by means of a simple reaction model. Such an uncontrolled methane formation can be avoided by adhering to the following protective measures: stirrer control, limitation of catalyst quantity and checking the thermal stability of starting materials and end products.

**Keywords:** hydrogenation, Raney nickel catalyst, runaway reaction

### I. Introduction

Amongst nickel catalysts, Raney nickel [1] is distinguished by its particularly high activity. It is obtained from finely ground Ni/Al alloy grains by leaching with highstrength caustic alkali, the aluminium being dissolved and a porous material of large specific surface area of about 80 m<sup>2</sup>/g remaining [2]. Since hydrogen is released on leaching, commercially available Raney nickel always retains large quantities of hydrogen. This catalyst is nowadays widely used industrially in liquid-phase hydrogenations.

### II. Plant accident

In a high-pressure hydrogenation, an unexpected pressure build-up occurred in a 1 m<sup>3</sup> hydrogenator, in which a polysubstituted acetonitrile dissolved in methanol was to be converted over the Raney nickel catalyst to the corresponding amine. The hydrogenation had been routinely carried out many times, without such a fault ever occurring. In this accident, the pressure rose towards the end of the hydrogenation within a few minutes from the hydrogen pressure held at 100 bar by pressure control up to 190 bar, and the temperature recorder showed a rise from 130° C to 160° C. However, there was no damage, since the autoclave was designed for the pressures and was protected by a relief valve. Due to a defect in the control unit, the stirrer had failed during this batch.

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A gas sample was taken from the gas phase of the autoclave while still in the cooling phase; this showed a pronounced depletion of hydrogen to about 1/3 of the quantity injected. On the other hand, the formation of hydrocarbons as well as CO<sub>2</sub> and CO was proved by gas chromatography:

H <sub>2</sub>	18 % by volume
CH <sub>4</sub>	65 % by volume
C <sub>2</sub> H <sub>6</sub>	0,6 % by volume
CH <sub>3</sub> OH	3,5 % by volume
CO <sub>2</sub>	4,2 % by volume
CO	6 % by volume
N <sub>2</sub>	1,4 % by volume

The hydrogenated material was examined for yield and quality, but no significant differences from earlier batches were found. The only noticeable point was a slight yellow coloration, whereas the solution was usually clear.

III. Laboratory investigations to explain the unexpected pressure build-up

Thermal stability of the hydrogenation material

The nitrile and amine were checked for thermal stability by means of differential thermal analysis. To ensure that possible catalytically active impurities were also detected, control measurements with an addition of 3 % of iron powder and iron(III) chloride powder and/or sodium hydroxide solution were carried out each time. Whereas the starting material and end product did not show any exothermic decomposition up to 400° C, the decomposition temperature was lowered down to 350° C by some of the additives. However, even this lowering is insufficient to explain the observed pressure build-up as the consequence of a decomposition reaction with heat release. Moreover, the unchanged quality of the hydrogenated material in the batch in question is an argument against any contribution by the hydrogenation reaction to the accident.

Proof of hydrogenation of methanol over Raney nickel

According to the above results, the unexpected pressure rise must have been caused by a reaction of the methanol solvent with the hydrogen over Raney nickel, and the investigations were concentrated on this point. They were mainly carried out in the 5 liter autoclaves used at Hoechst for adiabatic storage tests [3]. In addition, some experiments were also carried out in smaller autoclaves of 200 cm<sup>3</sup> capacity [4].

Experiments in the 5 liter autoclaves

In a first test series under 40 bar hydrogen pressure, 300 ml of methanol were stored with varying amounts of Raney nickel catalyst in a 400 cm<sup>3</sup> glass flask in the center of the autoclave. The catalyst was suspended in the methanol by means of a vertical reciprocating stirrer. If, however, stirring was omitted, the catalyst settled out at the bottom of the glass flask. The catalyst had previously been resaturated with hydrogen up to the saturation equilibrium at room temperature and atmospheric pressure, for which purpose H<sub>2</sub> was bubbled for a prolonged period through the

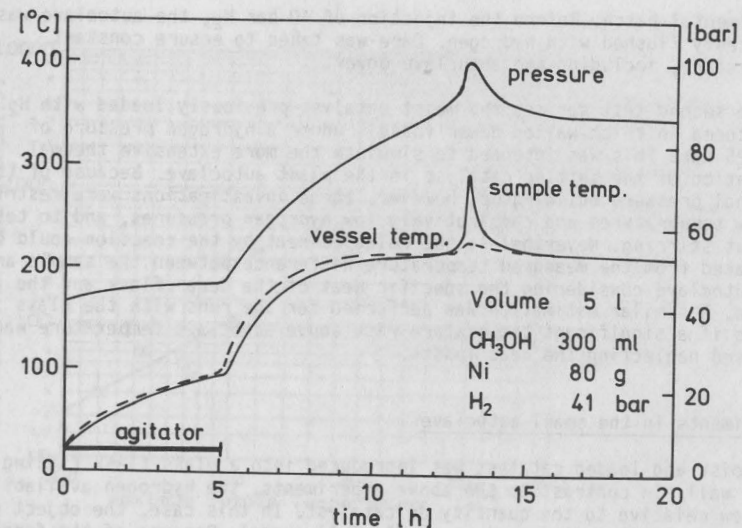


Figure 1: Temperature/pressure-time curve of run No. 4. The analysis of the gas phase yielded 60 % CH<sub>4</sub>, 1,2 % C<sub>2</sub>H<sub>6</sub> and 6 % CO<sub>2</sub>

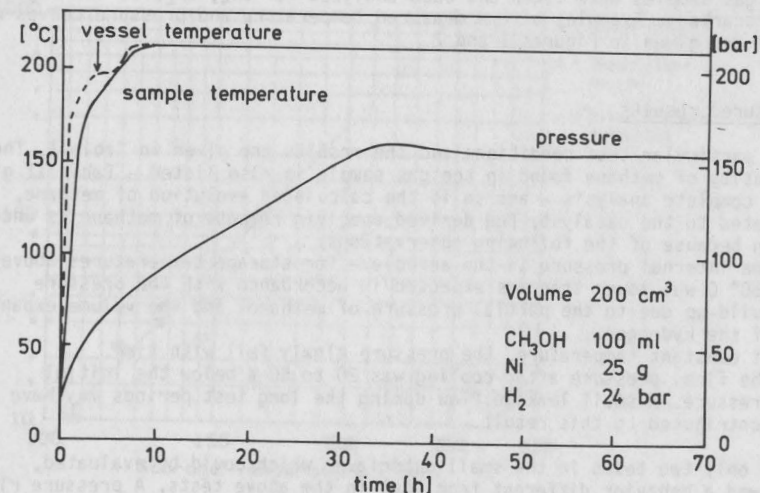


Figure 2: Temperature/pressure-time curve of run No. 13. The analysis of the gas phase yielded 41 % CH<sub>4</sub>, 10 % C<sub>2</sub>H<sub>6</sub>, 14 % C<sub>3</sub>H<sub>8</sub>, 5 % C<sub>4</sub>H<sub>10</sub>, 24 % CO<sub>2</sub> and 1,3 % H<sub>2</sub>

experimental batch. Before the injection of 40 bar H<sub>2</sub>, the autoclave was repeatedly flushed with hydrogen. Care was taken to ensure constant temperature, including the autoclave cover.

In the second test series, the moist catalyst previously loaded with H<sub>2</sub> was stored in thick-walled dewar vessels under a hydrogen pressure of 20 - 25 bar. This was intended to simulate the more extensive thermal insulation of the settled catalyst in the plant autoclave. Because of the methanol pressure building up, however, these investigations were restricted to low temperatures and comparatively low hydrogen pressures, and to tests without stirring. Nevertheless the released heat by the reaction could be estimated from the measured temperature difference between the sample and the autoclave considering the specific heat of the dewar flask and the sample. A similar estimation was performed for the runs with the glass flasks if a significant temperature rise above autoclave temperature was observed neglecting the heat losses.

Experiments in the small autoclave

The moist and loaded catalyst was introduced into a glass flask fitting the inner wall. In contrast to the above experiments, the hydrogen availability was low relative to the quantity of catalyst. In this case, the object was to simulate the conditions in a nearly full vessel. Because of the ferromagnetic properties of nickel, the otherwise usual magnetic stirring had to be omitted in these experiments.

The temperature of the sample, as compared with that of the interior of the autoclave, and the pressure were measured. After cooling of the autoclave, two gas samples were taken and each analyzed for CH<sub>4</sub>, CO<sub>2</sub>, CO and light hydrocarbons. Examples of the measured temperature and pressure curves with time are given in Figures 1 and 2.

Measured results

The particular test conditions and the results are given in Table I. The quantity of methane found in the gas sample is also listed - Table II gives the complete analysis - and so is the calculated evolution of methane, related to the catalyst. The derived specific release of methane is uncertain because of the following observations:

- The internal pressure in the autoclave for storage temperatures above 150° C was lower than was expected in accordance with the pressure build-up due to the partial pressure of methanol and the volume expansion of the hydrogen.
- At constant temperature, the pressure slowly fell with time.
- The final pressure after cooling was 20 to 50 % below the initial pressure. A small leakage flow during the long test periods may have contributed to this result.

The only two tests in the small autoclave, which could be evaluated, showed a behavior different from that in the above tests. A pressure rise persisting over several hours was observed (Figure 2). The final pressure was several times higher than the initial pressure. Apart from methane, the gas analysis showed high contents of higher alkanes as well as CO and CO<sub>2</sub>. The hydrogen was almost completely consumed.

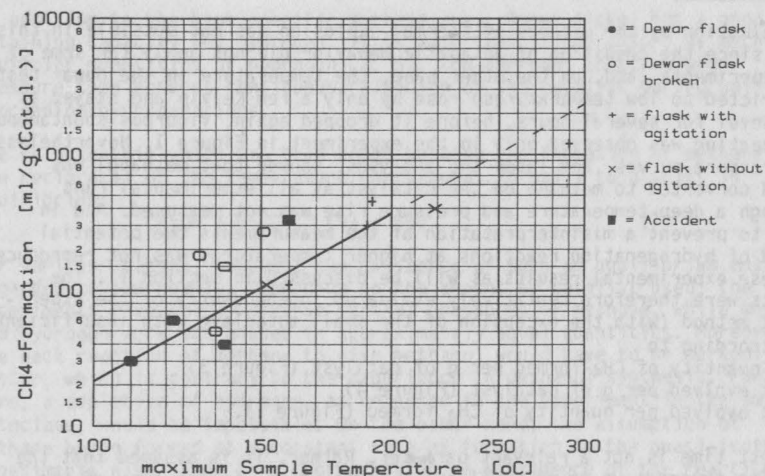


Figure 3: Methane formation from the reaction of methanol with hydrogen over Raney nickel

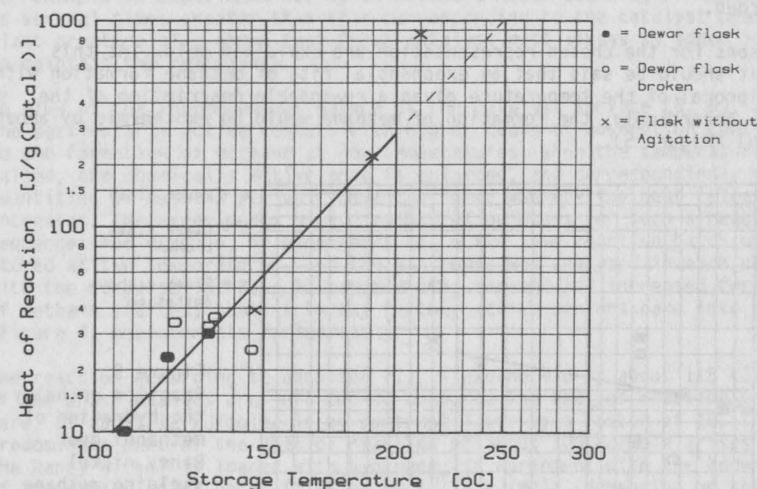


Figure 4: Heat of reaction of the hydration of methanol over Raney nickel

IV. Evaluation

An evaluation by the methods of thermal explosion was not possible in this case, since the condition of adiabatic behavior did not apply for some of the experiments, and, on the other hand, the temperature in the dewar tests (restricted to low temperatures) rose by only a few Kelvin and stayed at that level for several hours, before it dropped again. Vigorous spontaneous self-heating was observed only in the experiment in Figure 1. Nevertheless, the pressure curves, and later the analyses, showed that methanol was indeed converted to methane on the catalyst at all experimental runs although a deep temperature and pressure rise was not measured. And in order to prevent a misinterpretation of the measurements the potential hazard of hydrogenation reactions at higher temperatures was not reproduced by these experimental results as will be discussed in section VI. The results were therefore tentatively evaluated independently of the experimental method (with the exception of the small autoclave with insufficient H<sub>2</sub>) according to

- the quantity of CH<sub>4</sub> formed per g of catalyst (Figure 3)
- heat evolved per g of catalyst (Figure 4)
- heat evolved per quantity of CH<sub>4</sub> formed (Figure 5).

The test time is not a relevant parameter. Rather, it is assumed that the reaction proceeds up to an equilibrium state which, in the case of the quantity of methane formed, was related to the maximum sample temperature and, in the case of estimating the heat evolved, was related to the storage temperature. The heat of reaction is obtained from the ratio of the two derived results and relates to the respective temperature range. When fitting the straight line, the tests with the burst dewar and the plant accident, which were not adequately characterized by measurements, were disregarded.

The reasons for the chosen representation are explained below. At this point, it should be said that an exponential rise of methane formation with the reciprocal of the temperature gives a reasonable description of the results. Accordingly, the formation of methane would be exothermic by about 12 kJ/mol (Figure 5).

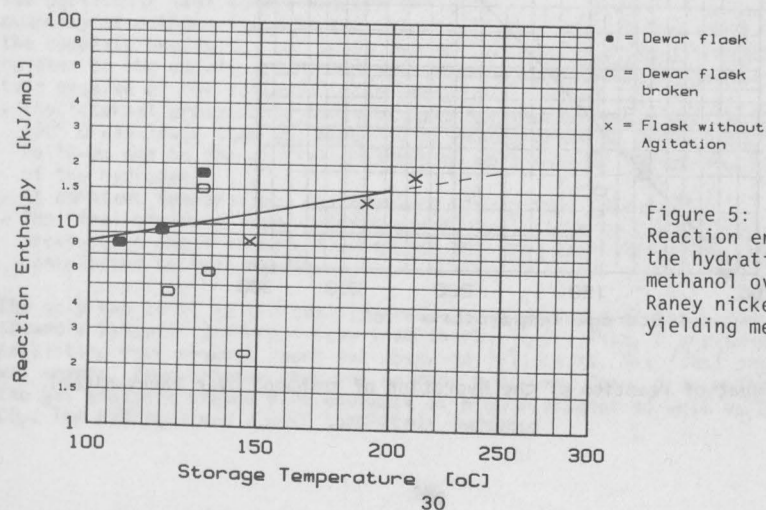
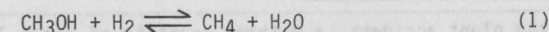


Figure 5: Reaction enthalpy of the hydration of methanol over Raney nickel yielding methane

V. Discussion

In addition to the high specific surface area, Raney nickel has a good retaining capacity for hydrogen. It is said that it can absorb as much as equimolar quantities of hydrogen [2, 5]. The hydrogen injected under pressure then ensures continuous reloading of the catalyst during uniformly proceeding hydrogenations.

The relationship which has been found between the formation of methane and the reciprocal of the temperature corresponds formally to a shift in equilibrium:



For various reasons, however, the existence of such an equilibrium must be regarded as improbable. Depending on the amount of catalyst used, the experiments gave fairly diverse partial pressures of methane, while methanol and hydrogen were introduced in approximately equal quantities. Moreover, the back reaction of methane to give methanol would have to be markedly faster, which is contrary to the experience in methanol synthesis. Furthermore, a depletion of hydrogen, as detected in the experiment in the small autoclave, would be impossible. On the other hand, the assumption of methane being formed at a constant rate of formation in the quasi-isothermal experiments also leads to a contradiction: a subsidence of the reaction with time was clearly observed (for example Figure 1).

A plausible explanation of the results is conceivable only under the assumption that poisoning of the catalyst proceeds in parallel with the formation of methane. This poisoning process must be slow as compared with the formation reaction of methane, since otherwise it would not be possible, for example in experiment No. 4, to detect a molar quantity of methane which is several times greater than that corresponding to the catalyst present. Plant practice also shows that fresh catalyst must always be added in order to maintain the reactivity.

In view of the inhomogeneous nature of the catalyst surface [5, 6], only the particularly active centers with higher heats of adsorption contribute to the formation of methane at low temperatures. When the temperature is raised, the chemically active area is enlarged, and correspondingly greater quantities of methane per unit time can form, whereby the heat release also increases. The experiments give a number of pointers for such a reaction sequence: for example, in experiment No. 5 the same reaction batch was stored at two temperatures, and the gas phase was analyzed in each case. With the stepwise increase in temperature, renewed and increased formation of methane started, that is to say further active centers came into play (Figure 4, measurements marked x).

The reaction according to equation (1) is exothermic by about 115 kJ/mole, if the phase changes are left out of account. The heat of reaction observed here, of about 12 kJ/mole, is by contrast lower by a factor of 10. The predominant part of the heat of reaction of about 100 kJ/mole arises when the Raney nickel is loaded with hydrogen, in agreement with the known heat of adsorption of H<sub>2</sub> on Ni films of 90 - 120 kJ/mole (depending on the surface cover [6]).

Bock has demonstrated that Raney Nickel leads to a selective elimination of hydrogen from an alcohol even at temperatures around 100° C: formation of acetone from propanol [7]. Here in a first, perhaps rate-determining

step, methanol releases a hydrogen molecule, and this is rapidly followed by the elimination of a further hydrogen molecule. The two reaction steps are thermally neutral if the high heat of adsorption of the hydrogen released is added in. The synthesis of methane from CO and H<sub>2</sub> would then correspond to the conventional use of Raney nickel in the detoxification of synthetic gas. Whether CO itself or an unduly fast hydrogenation without sufficient replenishing with hydrogen leads to poisoning of the catalyst must remain a speculation.

VI. Application of the plant accident

In the case of the plant accident, a methane quantity of about 70 % of the equimolar quantity of catalyst was detected, i.e. the rapidly available quantity of stored hydrogen was completely converted. Since, within the short time, reloading of the catalyst from the gas phase proceeded at a negligibly slow rate, the pressure rose due to the release of methane. The temperature increase additionally contributed via the rise in the partial pressure of methanol. Contrary to what would be expected from this investigation, however, a greater quantity of methane was formed; a possible reason may be that the measured maximum temperature was too low.

Self-heating as extensive as in the plant accident was not observed in the laboratory experiment. The heat build-up conditions applying in the settled catalyst in the plant vessel were not reproducible in the laboratory experiment. The plant accident thus corresponds to the most unfavorable case where the formation of methane comes to a stop only when the retained hydrogen has been consumed. The decrease in activity of the catalyst with increasing conversion was more than compensated by the gain in active centers due to the rise in temperature.

VII. Conclusions regarding the safety of hydrogenation reactions

The investigation has shown that a small quantity of methane is always evolved at relatively high hydrogenation temperatures, which was proved by GC analysis for the same hydration reaction afterwards. This passes unnoticed, since there is no increase in gas volume during the slowly proceeding reaction. By contrast, a runaway reaction is possible in the event of an accident, for example stirrer failure. Safe reaction control must therefore endeavor, by means of temperature control or restriction of the catalyst quantity, to limit the potential heat release in the event of an accident.

1. Stirrer control: Since it is known that Raney nickel can have a dehydrating action in the event of stirrer failure and can thus lead to an uncontrolled rise in temperature, stirrer control is necessary. Failure must trigger an alarm, so that countermeasures can be taken in good time.

2. Temperature limitation: The gradient of heat production must be smaller than the specific heat of the mixture.

$$d/dt \Delta H (\text{CH}_3\text{OH} + \text{H}_2 \longrightarrow \text{CH}_4 + \text{H}_2\text{O}) < C_p (\text{Mixture})$$

For a safe design, however, the heat release should be increased by the heat of adsorption due to hydrogen diffusion in later; somewhat arbitrarily, an additional 50 kJ/mole of methane is assumed for this.

Parts by weight Methanol : Catalyst		Specific heat C <sub>p</sub> [J/K/g(catalyst)]	Temperature limit for safe working	
			T <sub>1</sub> [° C]	T <sub>2</sub> [° C]
5	1	13,2	225	160
3	1	8,0	200	145
2	1	5,4	185	130
1	1	2,8	160	115
0	1	0,2	90	55

T<sub>1</sub> = relative to a heat of reaction of 12 kJ/mole  
T<sub>2</sub> = relative to a heat of reaction of 60 kJ/mole

This condition was not met in the settled catalyst during the plant accident, nor in the laboratory experiments without stirring.

3. Limiting the quantity of catalyst: The quantity of hydrogen retained on the nickel can lead to a spontaneous evolution of methane of 200 standard liters/kg of nickel. If settling of the catalyst must be expected at temperatures of around and above 90° C (see above), a possible pressure build-up must be limited by restricting the quantity of catalyst to a level in line with the strength of the equipment. For the example of a 1 m<sup>3</sup> autoclave with a free gas space of 0,4 m<sup>3</sup> at a permissible pressure rise by 20 bar and at a working temperature of 150° C, the amount of catalyst should be below 25 kg.

4. Checking the thermal stability of the reactants: The above calculations do not allow for any possible production of heat by the desired hydrogenation reaction or by the decomposition of the reactants in the event of an accident. Particular care is necessary in the case of aromatic nitro compounds, where there is a risk of a highly exothermic disproportionation [9, 10].

5. Change of solvent: The present investigation is restricted to methanol as the solvent. The results are not transferable without restriction to other solvents. In such a case, a further investigation will be necessary.

Acknowledgements

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## Reference

- [1] Raney, N., US Patent 1, 628, 191 (1927)
- [2] Fouillour, P., Applied Catalysis 8, 1 - 42 (1983)
- [3] Grewer, Th., Chem. Ing. Techn. 51, 928 (1979)
- [4] Klais, O. and Th. Grewer, Loss Prevention, C24, EFCE Publication Series No. 33 (1983)
- [5] Beek, O., Advances in Catalysis 2, 151 (1950)
- [6] Eucken, A., Advances in Catalysis 2, 156 (1950)
- [7] Bock, H. and H.P. Wolf, Ang. Chemie, 97, 411 (1985)
- [8] Palm, A., Winnecker-Küchler, Chem. Technologie, Volume 3, pp 359 (1972)
- [9] Kosak, J.R. in Catalysis in organic Syntheses, pp 107, Academic Press (1980)
- [10] Tong, W.R., R.L. Scagraves and R. Wiederhorn, Chemical Engineering Progress, Loss Prevention, Vol. II, pp 71 (1977)

Table I: Results of the experimental investigation

Nr.	Methanol [ml]	Raney-Nickel [g]	Hydrogen- pressure [bar]	Volume pressure- vessel [l]	Agita- tion	Temperature [°C]	time of experi- ment [h]	max. sample temp. [°C]	max. pressure [bar]	P <sub>initial</sub> / P <sub>final</sub>	CH <sub>4</sub> - concn- ratio [Vol.-%]	specific CH <sub>4</sub> -for- [l/g]l
Storage tests in open flask:												
1	300	80	40	5	yes	190	7	190	72	0,8	14,3	0,3
2	300	2,7	40	5	yes	192	16	192	71	0,7	1	0,45
3	300	80	41	5	yes	160	215	160	56	0,6	6,4	0,11
4	300	80	41	5	up to 100°C	210	20	290	102	0,8	60	1,2
5a)	200	80	65	5	no	147		152	89	-	2,9	0,11
b)	same sample											
13	100	ca.25	24	0,2	no	190	50	219	75	0,5	22	0,4
14	50	ca.15	24	0,2	no	208	12	208	114	2	41	0,14 <sup>2)</sup>
Storage tests in Dewar flask:												
6	100	100	11,3	5	no	122	110	130	20,4	-	25	0,18 <sup>4)</sup>
7	100	84	11,6	5	no	146	140	151	27,8	-	35	0,27 <sup>4)</sup>
8	100	82	11,6	5	no	132	90	138	25,2	-	5,5	0,04
9	120	45	11,3	5	no	132	24	135	24,2	-	3,4	0,05 <sup>4)</sup>
10	120	40	11	5	no	120	80	122	20,7	-	4,2	0,06
11	100	85	11	5	no	108	70	110	17,7	-	4,4	0,03
12	120	51	11	5	no	134	100	138	23,5	-	13	0,15 <sup>4)</sup>
Accident:												
	ca.300kg	ca.70kg	100	1000	yes/no	130(?)		160(?)	190	-	65	0,33 <sup>3)</sup>

- 1) Amount of CH<sub>4</sub> (standard conditions) per weight of catalyst
- 2) Beside CH<sub>4</sub> large amounts of higher alkanes were found
- 3) A free gas volume of 500 l was assumed
- 4) Dewar flask blasted

Table II: Results of gaschromatographic analysis (Vol.-%)

No.	1	2	3	4	5a)	5b)	13	Accident
Methane	14,3	1,0	6,4	61/59	2,9	22	41	65
Ethane	0,2	< 0,1	0,1	1,2	< 0,1	0,8	10	0,6
Propane	< 0,1	< 0,1	0,1	0,8	< 0,1	< 0,1	14	
Butane	< 0,1						5	3,5
Methanol	0,9	1,2	0,8	0,5			1	18
Hydrogen	83	> 95	> 90	33	90	75	1,3	
N <sub>2</sub>	2,3	1,9	1,6	1,8			1,4	
O <sub>2</sub>	< 0,1	< 0,1	< 0,1	< 0,1			< 0,05	
CO	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	6,0
CO <sub>2</sub>	0,2	< 0,1	< 0,1	5,0/6,7	< 0,1	2,3	24	4,2
NF <sub>3</sub>	6	7	8	9	10	11	12	
Methane	5,5	35	25	3,4	4,2	4,4	13	
Hydrogen	90	46	64	98	97	92	73	
CO	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05	
CO <sub>2</sub>	0,3	0,7	0,25	0,4	0,07	< 0,05	0,25	

CASE STUDIES ON UNSTABLE SUBSTANCES

J Bond\*

Three case studies are given to demonstrate various aspects of hazards that should be determined during the initial development of a process, from the research stage to plant operation. The need for a formal assessment of hazards at the research stage is proposed.

INTRODUCTION

The development of a product passes through five distinct stages:-

- Research
- Process development
- Process design
- Construction of plant
- Operation of plant

A sixth stage, that of demolition of the plant, may also be added if the whole history of the product and plant is considered.

At the research stage it is necessary to identify hazards that can reasonably be foreseen in the lifetime of the plant. Hazards may be associated with:-

- Flammability
- Explosability
- Toxicity
- Thermal and pressure conditions
- Environmental problems

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