

DIRECT AMMONOLYSIS OF RAPESEED OIL TO ALKYLNITRILES AND GLYCERINE

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Aliphatic alkyl nitriles containing 12-24 carbon atoms are important intermediates to produce alkylamines and different nonionic surfactants and quaternary ammonium salts. They are usually prepared by ammonolysis of fatty acids, although it is also possible to obtain them directly from fats. Two versions of such processes were already described in the middle of 1930. In the first version<sup>1,2</sup> reaction was carried out in liquid ammonia at room temperature, and glycerine and appropriate amides were obtained as products. In the second version<sup>3,4</sup> fats were reacted with great excess of gaseous ammonia at 300-400°C in the presence of dehydration catalysts such as  $Al_2O_3$ ,  $ThO_2$ ,  $SiO_2$ . In this case appropriate nitriles were formed and yields of 60 to 98-100% were claimed. However, glycerine was not recovered. It was probably degraded and destruction products contaminated nitriles. As a result of glycerine loss these processes were uneconomical.

Recently, it was demonstrated that the direct ammonolysis of oils can be carried out in such a way that the process seems economical<sup>5,6</sup> and appropriate pilot plant was build by Hoechst. Reaction is carried out in the liquid phase with a gas ammonia excess at temperatures below 300°C. Salts of zinc with fatty acids or with alkylbenzenesulphonate acids are preferred as catalysts, and glycerine formed is quickly separated from reaction mixture by evaporation in ammonia stream. Yields claimed are relatively high and equal to 90-95% and 80-95% for nitriles and glycerine, respectively.

The aim of this work was to carry out the direct ammonolysis of oils in a batch reactor and to determine reaction conditions protected high yields of nitriles and glycerine.

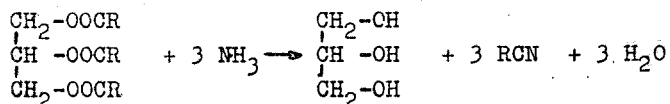
## EXPERIMENTAL

Rapeseed oil, tallow and gaseous ammonia were used as reagents, and zinc dodecylbenzenesulphonate as a catalyst. Reaction was carried out in a batch reactor passing ammonia through oil or molten fat, which contained appropriate amount of catalyst. Glycerine and nitriles formed were quickly distilled off and then separated. Reaction temperature was maintained in the range of 200-260°C. Gaseous ammonia flow was in the range of 200-800 dm<sup>3</sup> kg<sup>-1</sup> h<sup>-1</sup>, while the catalyst content was varied from 0.5% to 8% in relation to initial mass of oil.

Nitriles and amides were analysed by means of gas chromatography and potentiometric titration. Glycerine content was determined by means of titration using periodic acid<sup>9</sup>.

## RESULTS AND DISCUSSION

Rapeseed oil reacts with ammonia giving appropriate alkylnitriles, glycerine and water:



Depending upon reaction conditions undesired intermediate amides can also be formed. Thus, reaction conditions should be enough severe to convert fatty acids not into amides but fully into nitriles. Simultaneously, these conditions must be quite mild to avoid glycerine destruction or glycerine must be quickly and completely removed from reaction zone. This can be accomplished by appropriate selection of reaction conditions as well as by reactor design.

Reaction conditions and their influence on the yields of intermediate amides, final nitriles and glycerine are presented in Table 1. Figures 1 and 2 show the influence of the catalyst content and of reaction temperature on the content of amides in the nitrile fraction. They demonstrate that under considered conditions the effect of catalyst is very important for its concentration range below 2%. The ammonia flow rate which together with temperature decides

on the reaction time also significantly influences the amides' content. However, the process cannot be optimized considering the content of amides, if this was the case then too severe reaction conditions would be selected. As a result quite important amounts of glycerine would be destroyed and the process would be uneconomical.

The data given in Figs 3 and 4 demonstrate that temperatures below 220°C do not influence significantly the yield of glycerine. However, with further increase of temperature the yield of glycerine recovery distinctly decreases. Such increase of temperature is then possible in the second stage of the process, i.e. after removal of important glycerine amounts. Positive effects on the yields of products considered and the content of intermediate amides are also observed.

The effect of catalyst content depends upon reaction temperature and ammonia flow rate. In the region below 2% the increase of catalyst content causes important increase of the yields of nitriles and glycerine. With further catalyst content increase the change of the nitrile yield is relatively small but yield of glycerine significantly decreases. Thus, under considered reaction conditions the catalyst content should be about 2%. The use of heterogeneous ZnO as catalyst is disadvantageous and significantly lowers reaction yields. Products contain then important amounts of undesired intermediate amides.

#### CONCLUSIONS

Direct ammonolysis of rapeseed oil runs in relatively mild reaction conditions: temperature of 220-240°C, catalyst content of 2% and ammonia flow rate of 500 dm<sup>3</sup>kg<sup>-1</sup>h<sup>-1</sup>. Under such conditions it is possible to obtain yield of nitriles of 80-90% and yield of glycerine near 80%. Reaction products contain also 4-10% of intermediate amides which can easily be converted into nitriles in the second reaction stage after removal of glycerine.

Nitriles obtained are light in colour and glycerine is of sufficient quality.

#### Acknowledgment

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Table 1. Reaction conditions and yields of products

Temp.	Catalyst cont.	NH <sub>3</sub> rate	Flow rate	Reaction time	Amide cont.	Nitrile yield	Glycerine yield
°C.	%	dm <sup>3</sup> /kg h	h	%	%	%	
260	2	500	1.6	6.1	79.5	58.7	
240	2	500	2.8	4.7	84.1	60.7	
220	2	500	3.5 <sup>xx</sup>	5.4	87.4	78.9	
200	2	500	5.0 <sup>xx</sup>	4.1	86.4	76.0	
220	0.5	500	4.9 <sup>xx</sup>	21.0	78.7	68.1	
220	1	500	4.9 <sup>xx</sup>	13.9	87.5	74.9	
220	4	500	3.4 <sup>xx</sup>	5.8	84.6	72.1	
220	8	500	5.3	3.5	93.7	65.7	
240	1	500	3.6	11.9	84.2	66.5	
240	4	500	3.9	5.0	88.7	61.4	
260	4	500	1.2	3.2	82.5	47.1	
240	4	800	1.7	6.8	84.0	70.0	
220	4	800	3.8	11.4	84.3	77.0	
240	1 <sup>x</sup>	500	4.0	16.1	70.1	47.5	
240	1 <sup>x</sup>	800	3.6	20.5	51.0	48.7	

<sup>x</sup> - ZnO as a catalyst

<sup>xx</sup> - temperature of 240°C of the last hour of the process

#### REFERENCES

1. US Pat 2 070 991 (1937)
2. UK Pat 445 148 (1936)
3. UK Pat 416 631 (1934)
4. UK Pat 451 594 (1936)
5. GFR Pat 2 737 607 (1979)
6. GFR Pat 2 813 204 (1979)
7. GFR Pat 3 244 752 (1982)
8. S.Billenstein and G.Blaschke, J.Amer.Oil Chemists' Soc.,  
61, 353 (1984).
9. DGF Einheitsmethoden E-III 3a 55

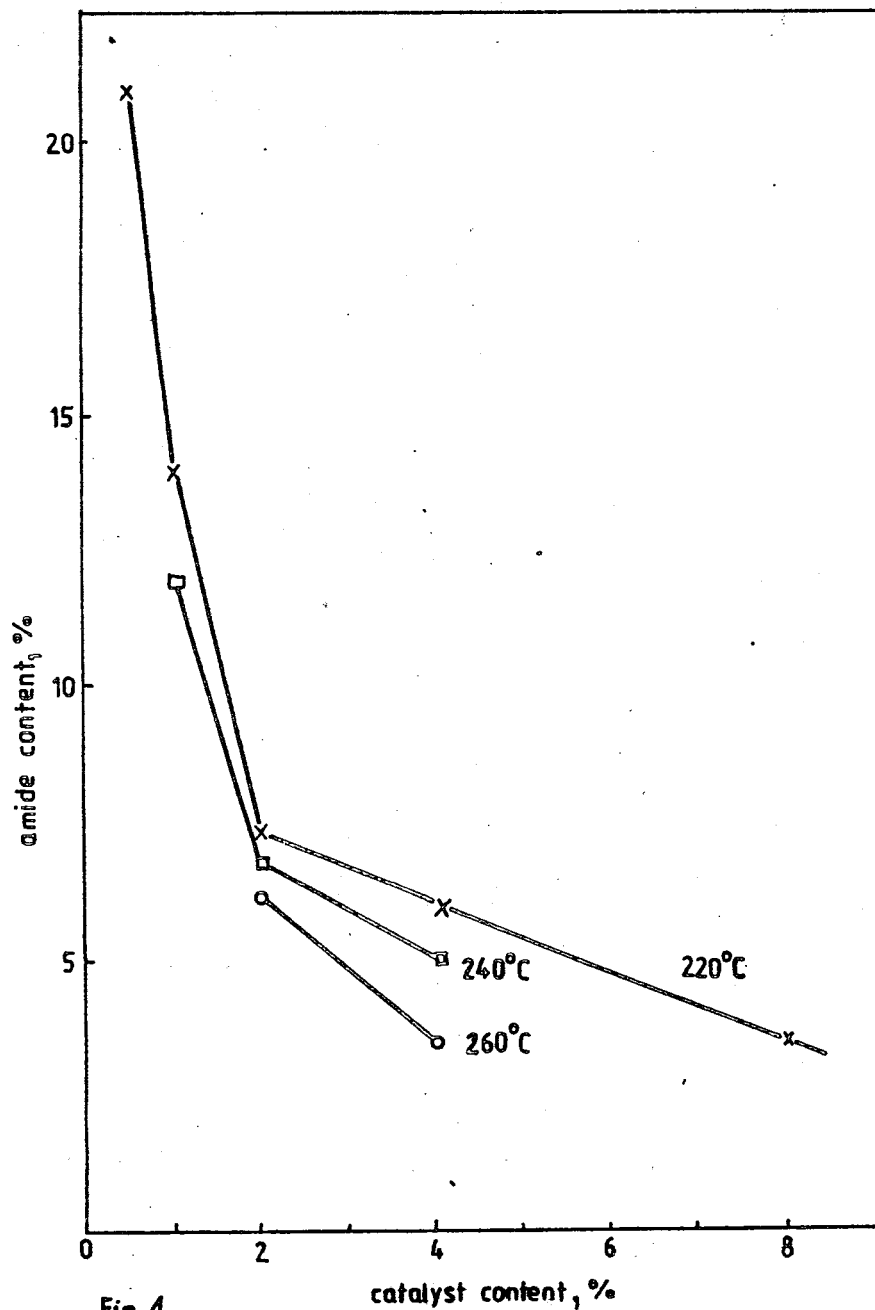


Fig. 1

Effect of catalyst on the amides content in the nitrile fraction ( $v_{\text{NH}_3} = 500 \text{ dm}^3/\text{kg h}$ )

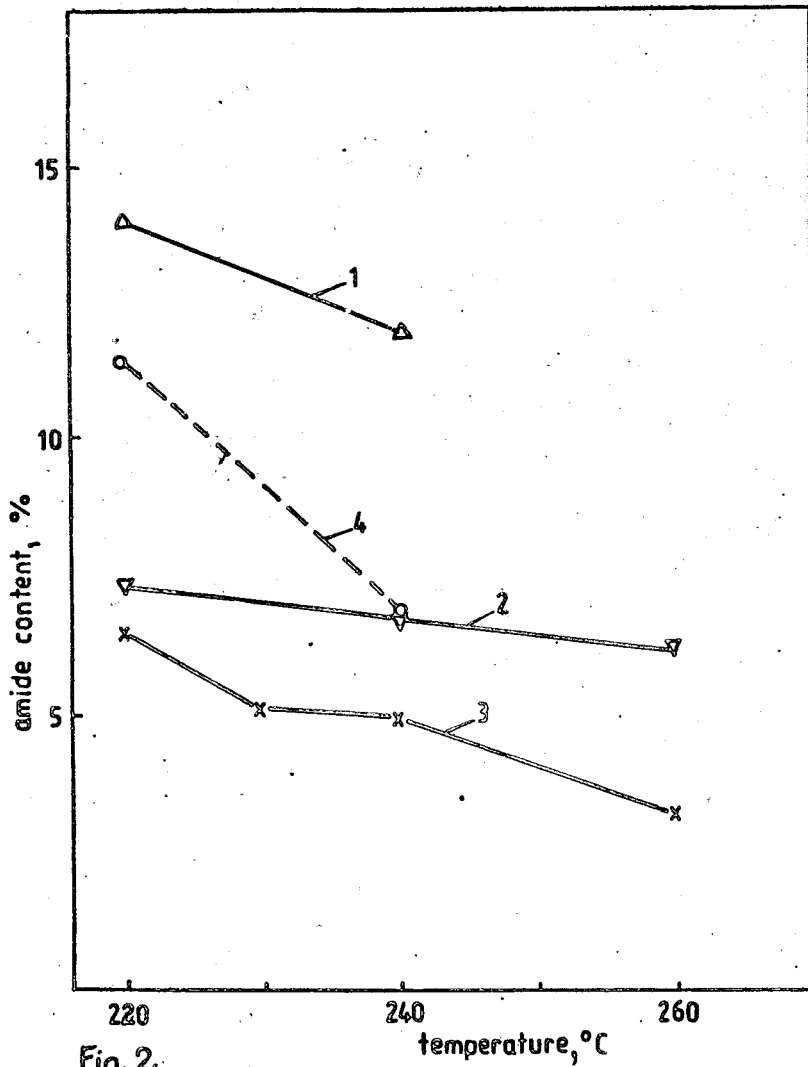


Fig. 2

Effect of temperature on the amides content in nitrile fraction (1,2,3 -  $v_{\text{NH}_3} = 500 \text{ dm}^3/\text{kg h}$ , 4-  $v_{\text{NH}_3} = 800 \text{ dm}^3/\text{kg h}$ , 1-  $c_{\text{cat}} = 1\%$ , 2-  $c_{\text{cat}} = 2\%$ , 3,4-  $c_{\text{cat}} = 4\%$ )

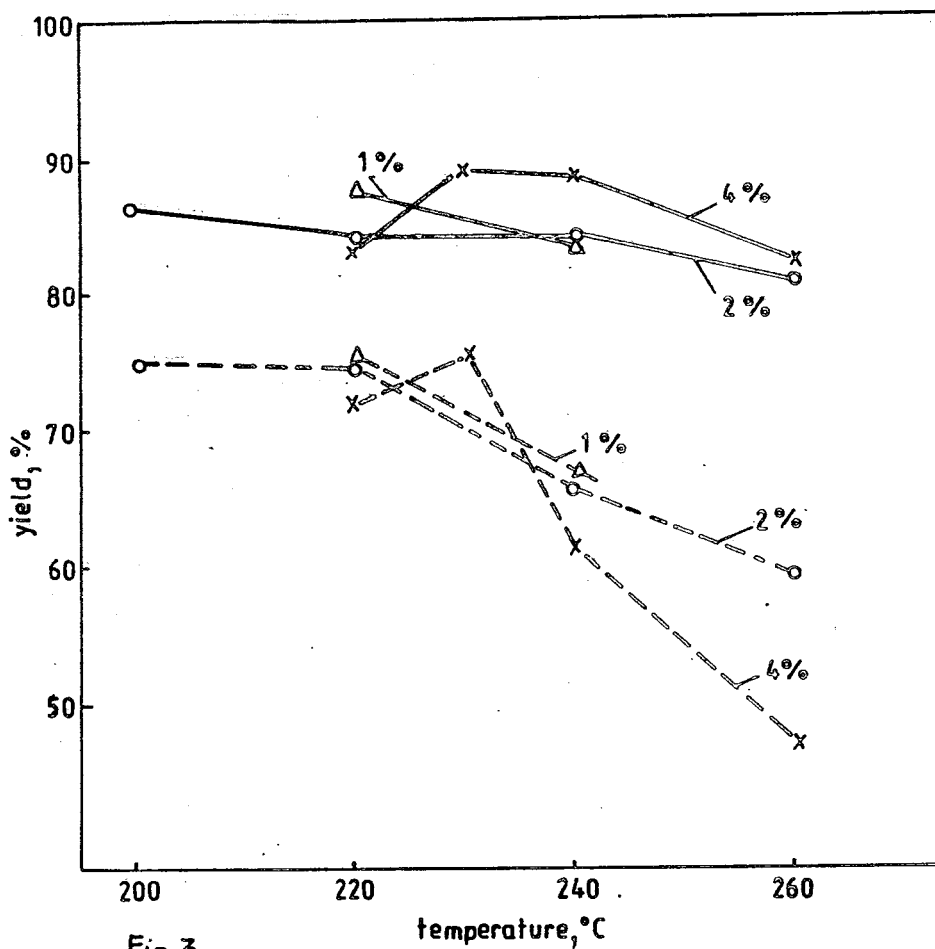


Fig.3

Effect of temperature on the yields of nitriles (—) and glycerine (---) for different values of catalyst content

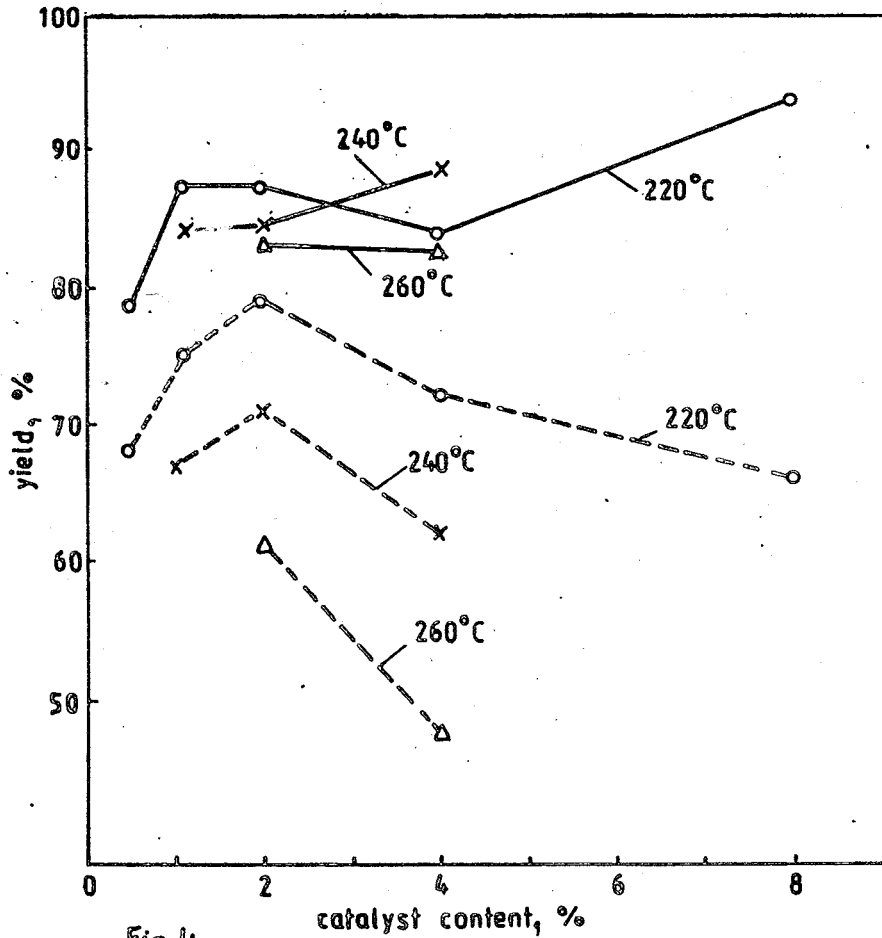


Fig. 4

Effect of catalyst content on the yields of nitriles (—) and glycerine (---)