PRODUCTION OF 3-METHYLPYRIDINE FROM ACROLEIN AND AMMONIUM SALTS IN SUB- AND SUPERCRITICAL WATER

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Glycerol, which is accumulated to a great extent as a by-product during fat saponification and biodiesel production, can be dehydrated into acrolein in sub- and supercritical water with high selectivities [1]. Acrolein, an important and versatile intermediate for the chemical industry, can further be converted to 3-methylpyridine, a source material for the production of insecticides, herbicides and vitamins. Up to now, the main production route is the heterogeneously catalysed gas phase conversion of acrolein with ammonia over alumina silicates and oxides with pyridine as a by-product. As an alternative route it could be shown that the addition of ammonium salts to aqueous acrolein solutions in hot compressed water (HCW) leads to considerable amounts of 3-methylpyridine with high space-time-yields. The experiments were conducted in *HCW* (125-350 °C, 25-35 MPa) using a high pressure apparatus with a plug-flow-reactor. The influence of residence time, temperature, pressure, different ammonium salts and concentrations were examined. A yield of 48 mol% of 3-methylpyridine is obtained at 225 °C, 30 MPa, 25 s residence time, 89 mmol L^{-1} ammonium acetate and nearly complete acrolein conversion. Similar yields can be achieved under related conditions with ammonium sulfate after 60 s residence time, indicating a strong dependence of the reaction rate on the p*H* value.

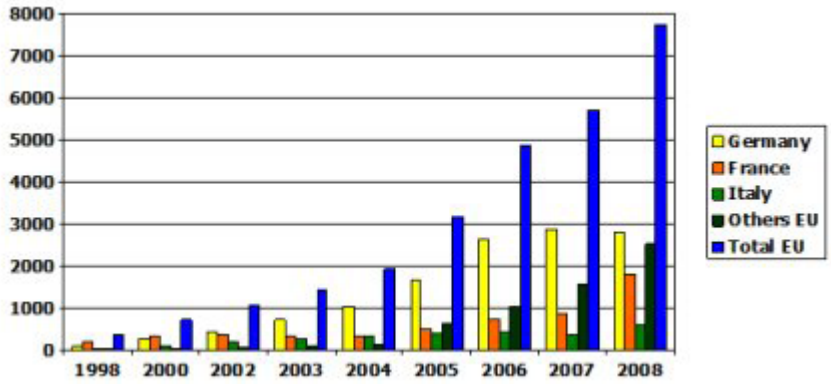
INTRODUCTION

The increasing CO_2 content in the air and the increasing demand of fossil raw materials makes the development of new chemical processes for the intermediates on the basis of renewable sources essential. Glycerol, a principle constituent of all fats and oils, is the major value-added by-product produced from oil and fat saponification such as transesterification reactions performed during oleochemical and biodiesel manufacturing processes. Increased global production of biodiesel since the late-1990s (see Fig. 1) has created an abundance of crude glycerol resulting in a decline in glycerol pricing [2]. Whereas between 2000 and 2003 the price moved in the range of 1000 to 1300 € t^{-1}, from 2004 to 2006 it decreased to 500 to 700 € t^{-1} [3]. Biodiesel production in the EU is forecasted to increase to about 12 million tons (Mt) in 2010, therefore about 1.2 Mt $annum^{-1}$ of additional pure glycerol will enter the European Market. Although there is already a great number of common glycerol applications like the usage in pharmaceuticals, cosmetics and foods, these markets are generally considered saturated making it difficult to extend the uses of glycerol in these areas. Such an abundant, renewable and inexpensive compound makes the development of processes to commercially valued chemicals desirable.

One of the chemicals into which glycerol can be converted is acrolein. In addition to the petrochemical route, acrolein can be gained by the gas or liquid phase dehydration of

glycerol. In heterogeneously catalysed processes zeolithes, aluminas, phosphor- or silicotungstic acids and acid salts are commonly used as catalysts leading to a yield of greater than 70 % at temperatures between 250 and 350 °C [3].

Figure 1 : EU27 and member states biodiesel production (`000 t) [4].



The dehydration of glycerol was also examined in sub- and supercritical water (T > 300 °C, P > 30 MPa), using either no catalyst or different additives (see Tab. 1). Ott, Bühler, Ramayya and their co-workers confirmed that the formation of acrolein was controlled by ionic species (such as protons) and can be increased by the presence of an acid and subcritical water conditions [1][5][6]. It was found that at lower temperatures, a carbonium ion mechanism results in the formation of acrolein, whereas a reverse aldol (retroaldolization) reaction to acetaldehyde and formaldehyde competes with the dehydration during the catalytic dehydration of glycerol. Watanabe et al. revealed that the yield of acrolein can be enhanced by a combination of higher pressures with higher concentrations of glycerol and sulphuric acid [7].

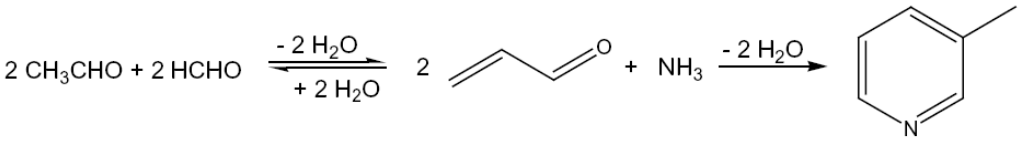
Table 1 : Yields of acrolein in sub- and supercritical water.

Catalyst/additive	Temperature / °C	Pressure / MPa	Yield / %	Literature
None	300-474	25-45	11	[5]
Sulfuric acid (5 mmol L^{-1})	300-350	34.5	47	[6]
Sulfuric acid (1-5 mmol L^{-1})	300-400	25-34.5	74	[7]
Zinc sulfate (470 ppm (g g^{-1}))	300-390	25-34	40	[1]

In addition to the use as a valuable intermediate for the production of acrylic acid, glutaraldehyde and methionine, acrolein can be utilized in the preparation of 3-methylpyridine.

A significant proportion of 3-methylpyridine is used as the starting material in the manufacture of pharmaceuticals and insecticides such as chlorpyrifos, feed additives such as nicotinic acid or nicotine carboxamide and herbicides like fluazifopbutyl [8]. The industrial synthesis of alkylpyridines is usually achieved by the addition-cyclization of aldehyde or ketone mixtures with ammonia. The reaction of acetaldehyde, formaldehyde and ammonia in the gas phase is used commercially for the manufacture of pyridine and 3-methylpyridine, getting approximately equal amounts of both substances [9]. The reaction can be directed to

give mainly pyridine by the addition of oxygen. Acetaldehyde and formaldehyde appear to first form acrolein, which reacts to 3-methylpyridine by condensation with ammonia (see (1)) [8].



(1)

The direct synthesis of the pyridines from acrolein over silica/alumina oxides supported catalysts give yields of 56 % of 3-methylpyridine and 26 % of pyridine [9]. The addition of propionaldehyde to the reaction mixture increases the yield of 3-methylpyridine [10].
The synthesis of simple alkyl pyridines in the liquid phase were reported by Grayson et al. [11]. Mainly mixtures of acetaldehyde and formaldehyde and their acetals and polymers were converted in ammonium salts containing solutions, organic amides, or alkali metal salts in the presence of aqueous ammonia. Acrolein and crotonaldehyde were also investigated as alternative starting materials, in pure form or in mixtures with formaldehyde, acetaldehyde, or paraldehyde. The reactions were carried out in an autoclave at 230 °C and a 3.4 mol L^{-1} diammonium hydrogensulfate solution. The addition of acrolein to the solution over a period of 36 min gave 55 % yield of 3-methylpyridine with little pyridine formation. The product contribution is the same as that produced by an equivalent mixture of acetaldehyde and formaldehyde.
Another reported successful condensation of acrolein with ammonia in the liquid phase was performed in aqueous propionic acid [12]. 3-Methylpyridine could be isolated in 33 % yield.
Previous papers only reported on the polymerisation of the acrolein [13].
This work deals with the further treatment of the acrolein produced by the dehydration of glycerol to 3-methylpyridine. In particular, we focuss on the optimisation of the reaction with ammonium salts under continuous conditions, short residence times and pressures comparable to the dehydration step.

MATERIALS AND METHODS

High pressure plant

The experiments were performed in a high pressure apparatus with tube reactors made of INCONEL® alloy 625 (specification 2.4856, with capacities of 4.4 cm³ and 49.5 cm³ respectively). The maximum possible working conditions of this apparatus are 40 MPa and 400 °C, with measured residence times between 5 and 240 s. The acrolein and the ammonium salt solutions were fed into the reactor via two separate preheated lines. Detailed description of the high pressure plant is given elsewhere [14].

Analytic

The content of the pyridines was determined by GC-FID (DANI Model 1000, capillary-column: CW 20M CB, CS, L = 25 m, d_i = 0.32 mm, d_f = 0.5 µm). The reactor sample was

diluted with 2-propanol in a 1:2 (g g^{-1}) ratio to obtain a homogeneously evaporation of the sample. 3,5-dimethylpyridine was used as the internal standard and ammonia water was added to bring the solution to pH > 7. The aldehydes were analyzed by GC-FID (Shimadzu Model 17 A, capillary-column: OV 1701-CB, CS, L = 25 m, d_i = 0.32 mm, d_f = 0.5 µm). Dilution was carried out with 2-propanol in the same ratio, containing 1-butanol as the internal standard and o-((2,3,4,5,6)-pentafluorobenzyl)hydroxylamine hydrochloride as the derivization agent.

RESULTS

The conversion of 0,25 % (g g^{-1}) acrolein in HCW with ammonium salts was investigated by varying the following process parameters:

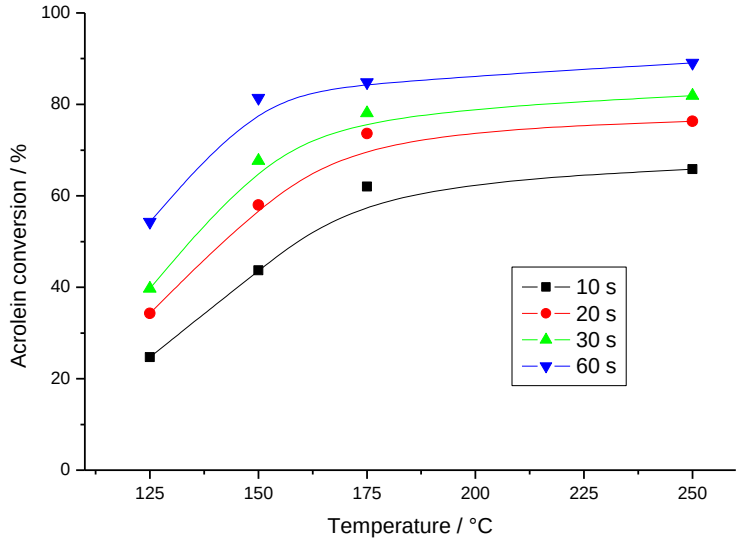
- temperature
- pressure
- ammonium salt
- ammonium salt concentration
- residence time

The feed concentration was chosen so that it corresponded to the highest self measured yield of acrolein by dehydration of 1 % (g g^{-1}) glycerol and avoiding occasional plugging of the plant.

Influence of the temperature

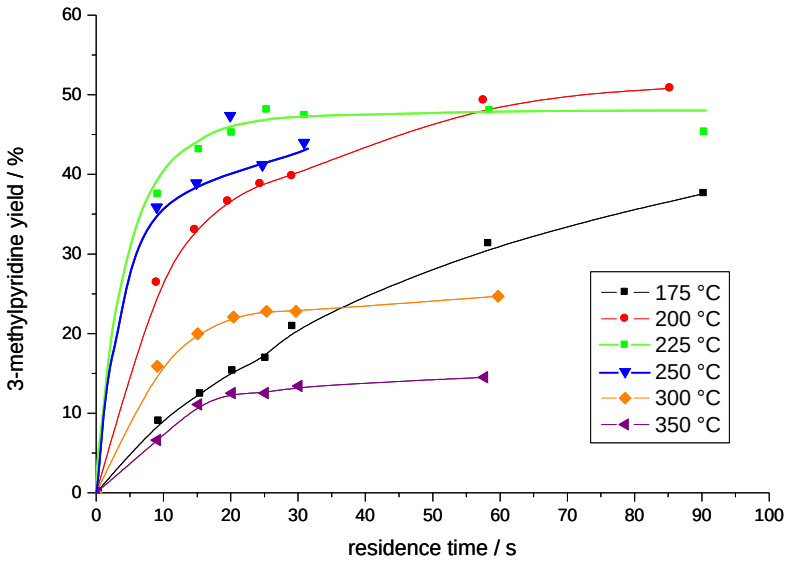
Fig. 2 shows the influence of the temperature with respect to the conversion of acrolein at a constant pressure of 30 MPa. The concentration of ammonium sulfate was 44 mmol L^{-1} and was equimolar to the acrolein concentration. The acrolein conversion increases strongly until 175 °C, whereas at temperatures above 175 °C a slightly increasing conversion is apparent. In comparison, the conversion is always above 90 % with 89 mmol L^{-1}ammonium acetate as ammonia supplier at the same conditions, indicating a pH dependence of the reaction.

Figure 2 : Temperature influence on the acrolein conversion at 30 MPa and 44 mmol L^{-1} ammonium sulfate concentration.



The influence of the temperature in a range from 175-350 °C on the 3-methylpyridine yield at 30 MPa and 89 mmol L^{-1}ammonium acetate can be seen in Fig. 3. An increase of the yield with increasing temperature is visible up to 225 °C. Above this temperature the yield decreases due to side reactions of acrolein.

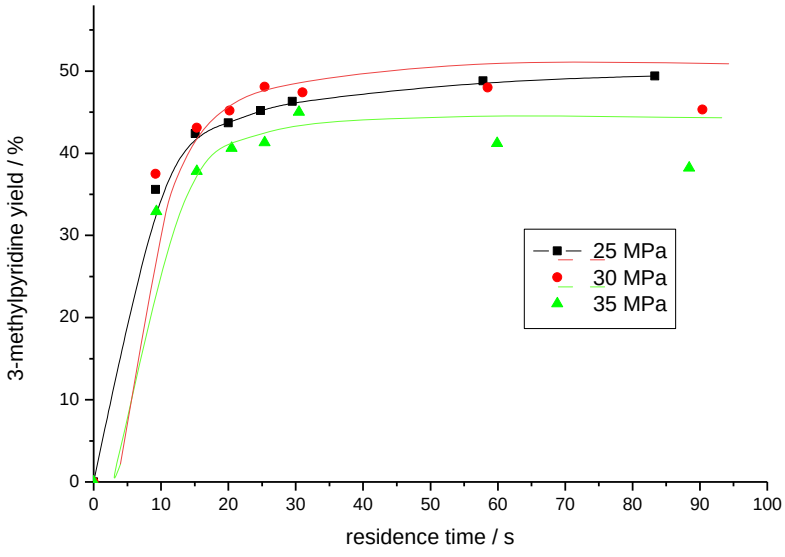
Figure 3 : Influence of the temperature range175-350 °C and influence time at 30 MPa and 89 mmol L^{-1} ammonium acetate concentration in terms of 3-methylypridine yield.



Influence of the pressure

Fig. 4 shows the dependency of the 3-methylypridine yield on the pressure and residence time. The effect of pressure becomes visible only above 30 MPa, when the 3-methylypridine yield slightly decreases.

Figure 4 : Pressure influence on the 3-methylypridine yield at 225 °C and 89 mmol L^{-1} ammonium acetate concentration



Influence of the ammonium salt

The dependency of the 3-methylpyridine yield at 30 MPa and 250 °C on the type of ammonium salt can be seen in Fig. 5. High yields in short residence times are obtained using ammonium acetate. Taking acid salts like ammonium hydrogen sulfate and diammonium hydrogen phosphate leads to slower formation of 3-methylpyridine. The reason is the slower conversion of acrolein, illustrated by Fig. 6, where the conversion of acrolein is plotted against the retention time at the same conditions. A stabilizing effect of protons on acrolein conversion is assumed.

Figure 5 : Influence of the ammonium salt on the yield of 3-methylpyridine at 250 °C and 30 MPa The concentration of the ammonium salts are 44 mmol L^{-1} for ammonium sulfate and 89 mmol L^{-1} for ammonium acetate, diammonium hydrogen phosphate and ammonium hydrogen sulfate.

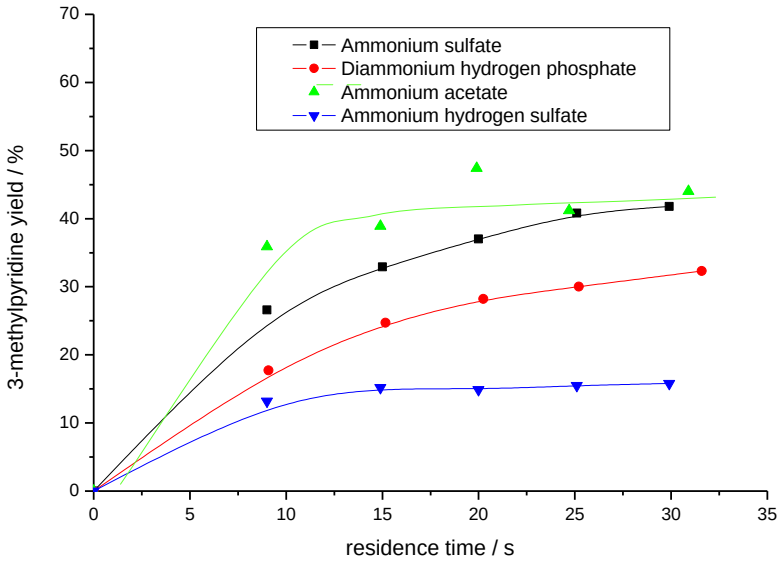
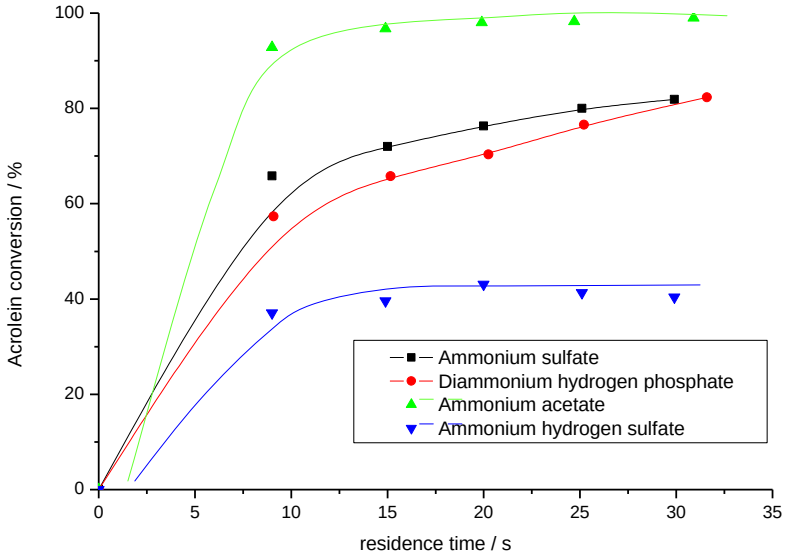


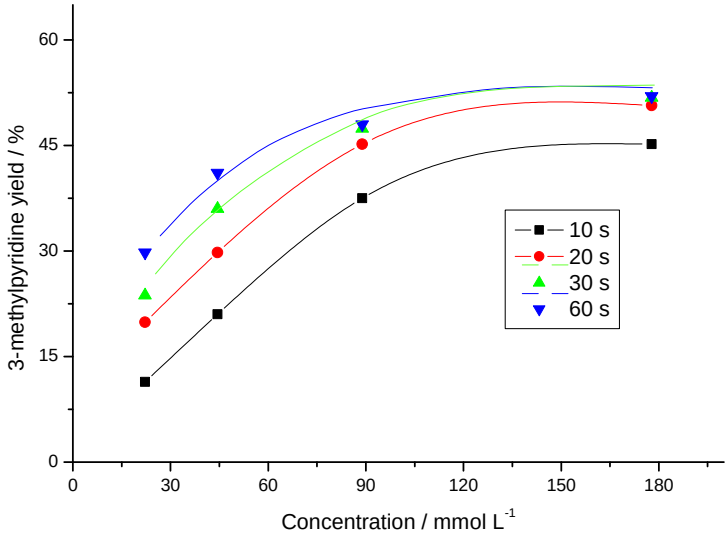
Figure 6 : Influence of the ammonium salt on the conversion of acrolein at 250 °C and 30 MPa. The concentration of the ammonium salts are 44 mmol L^{-1} for ammonium sulfate and 89 mmol L^{-1} for ammonium acetate, diammonium hydrogen phosphate and ammonium hydrogen sulfate..



Influence of the ammonium salt concentration

High yields of 3-methylpyridine by the cyclization of acrolein in *HCW* can be obtained with the excess of ammonium salt. Fig. 7 shows the dependence of the 3-methylpyridine yield on the concentration of the ammonium acetate concentration at different residence times. A significant increase of the yield is visible up to four times the stoichiometric excess (88.9 mmol L^{-1}) of the ammonium salt for all residence times.

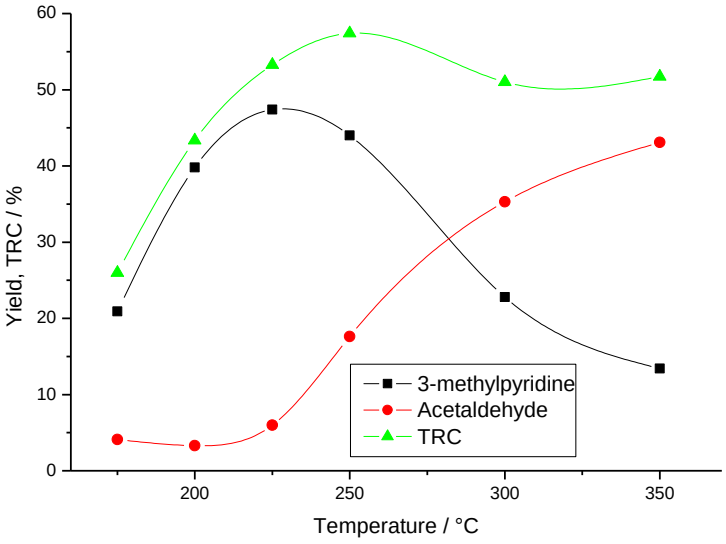
Figure 7 : Influence of the initial ammonium acetate concentration at 225 °C and 30 MPa on the 3-methyl-pyridine yield.



By-products and total carbon balance

In addition to acetaldehyde, formaldehyde and pyridine gaseous by-products like carbon dioxide, carbon monoxide and methane could be detected via infrared spectroscopy. A quantification of the gases was not possible due to very low gas flows. The gases were produced by the cleavage of formaldehyde and acetaldehyde, which could be verified by stability investigations of the aldehydes. Experiments on the stability of 3-metyhlpyridine at 360 °C, 30 MPa and 80-240 s residence time showed no conversion of the main product.
The total recovered carbon (*TRC*) and the yields of 3-methylypridine and acetaldehyde are plotted against the temperature in Fig. 8. The optimum condition for the production of 3-methylypridine with ammonium acetate is around 225 °C, whereas high yields of acetaldehyde are obtained at 350 °C. Between this temperature range, the carbon recovery of the chemical analysis was between 50 and 60 %. At temperatures below 200 °C the formation of oligomers and polymers of acrolein probably occurred, but were not detectable. At temperatures above 350 °C mostly gaseous products were formed. The maximum yield of pyridine was 3 % for all experiments.

Figure 8 : Yields of 3-methylypridine and acetaldehyde and total recovered carbon plotted against the temperature at 30 MPa, 30 s residence time and 89 mmol L^{-1} ammonium acetate concentration.

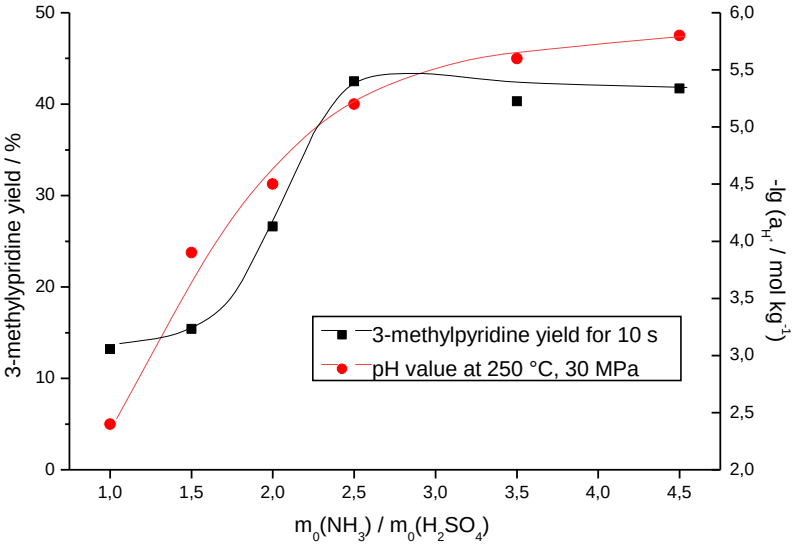


CONCLUSION

The use of ammonium salts leads to high yields in the cyclization reaction of acrolein to 3-methylpyridine and is an alternative for the industrial production in the gas phase. The formation rate of the pyridine derivate is dependent on the p*H* value under reaction conditions. Fig. 9 illustrates the comparison of the 3-methylpyridine yield at 250 °C and 30 MPa with the calculated p*H* value of aqueous ammonia/sulphuric acid mixtures under the same conditions with different initial molal ratios of the substances [15]. In this example, the transition from acidic to alkaline and inversely proceeds at a pH value of about 5.5, because

the pK_w value of pure water is 10.98 under these conditions. An increase of the yield with higher pH values is visible in the acidic area, whereas further addition of the base does not leads to higher yields. The selectivity remains constant over the entire pH-range and therefore the assumption that protons are inhibiting the acrolein conversion is confirmed.
The shown results make a direct synthesis of 3-methypyridine from glycerol in a two-step reaction conceivable, whereas the ammonium salt can be added between the first step of dehydration of glycerol and the second step of cyclization of the produced acrolein. The continuous processing of the dehydration solution in short residence times without relaxation makes the application particularly interesting. Acetaldehyde and formaldehyde are obtained as main by-products and can be refed into an industrial utilization to produce acrolein [11]. So far, the dehydration reaction was limited to a maximum glycerol concentration of 5 % (g g^{-1}), because otherwise plugging (coking) occurred. Further investigations have to be carried out to increase the initial concentration and to make the process industrially applicable.

Figure 9 : Comparison of the 3-methylypyridine yield (250 °C, 30 MPa, 10 s residence time) with the pH value of aqueous ammonia/sulphuric acid solutions at different initial molal ratios of ammonia to sulphuric acid (constant initial sulphuric acid concentration of 44 mmol kg^{-1}).



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