

## ALKALI SALTS IN HYDROTHERMAL BIOMASS GASIFICATION: CHANCE AND CHALLENGE

A. Kruse\*, D. Forchheim, F. Ottinger, J. Zimmermann,  
ITC-CPV, Forschungszentrum Karlsruhe, Hermann-von-Helmholtz-Platz 1,  
76344 Eggenstein-Leopoldshafen, Germany.  
Phone: +49 7247 823388 , Fax: +49 7247 822244  
Andrea.kruse@itc-cpv.fzk.de

The hydrothermal gasification of wet biomass is a promising process to use biomass residues of high water content [1]. Here “green” biomass can be converted without prior drying. Recently important improvements are accomplished, but still challenges in view of the technical application exists. One of the most important challenges is the handling of salts as natural ingredients of biomass. In subcritical processes, some salts poison the heterogeneous catalyst being necessary for the conversion. In supercritical processes, the solubility of salts is decreased and therefore plugging by salt deposition occurs [1]. Here diverse salts behave different [2]: So-called type 1 salts do not form solid deposition but a second salt-rich aqueous phase (hydrothermal brine). Recently in studies of supercritical water gasification, hydrothermal brines are produced which fulfil the following roles [3]:

- 1) catalytic medium,
- 2) a “catcher” for salts, which may cause plugging
- 3) an “ionic liquid” for biomass conversion.

In this study, some salts were successfully captured by the hydrothermal brine. A disadvantage was that also unwanted side reactions are supported by the high salt content in the hydrothermal brine.

### INTRODUCTION

One of the most important challenges is the handling of salts as natural ingredients of biomass. In subcritical processes, some salts poison the heterogeneous catalyst being necessary for the conversion. In supercritical processes, the solubility of salts is decreased and therefore plugging by salt deposition occurs. Here diverse salts behave different: So-called type 1 salts do not form solid deposition but a second salt-rich aqueous phase. This second fluid is named “hydrothermal brine” in the following. Such brines pass tubular reactors without retention but not necessarily reaction vessels.

On the other hand, the presence of salts show also advantages. Alkali salts are effective catalysts for the water-gas shift reaction [4]:  $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$  (1)

Only in the presence of such salts, high hydrogen yields at reasonable reaction times are possible. Indirectly by this catalysis also unwanted side reactions, namely polymerisations are avoided because by the water-gas shift reaction active hydrogen is formed, reacting with precursors for tar/coke formation.

Figure 1 shows the influence of salts, here shown for glucose as salt free model substance for biomass. The addition of salts increases the gas yield and changes the gas composition. The CO content is lower and the H<sub>2</sub> and CO<sub>2</sub> content higher in the presence of an alkali salt. The salts in biomass show nearly the same effect like the addition of salts to glucose.

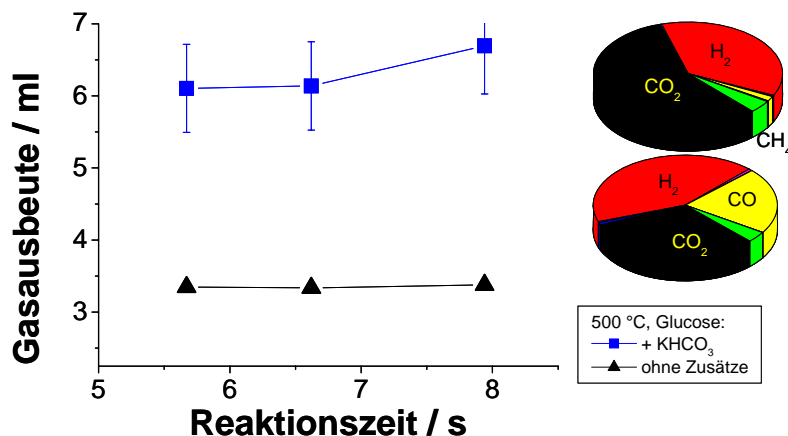


Fig.1: Gas yield of Glucose gasification as function of reaction time with and without the addition of  $\text{KHCO}_3$  (2 % (g/g) Glucose, 0.2 % (g/g)  $\text{KHCO}_3$ , 26 MPa, tubular reactor). Additionally the gas composition reached is shown [5].

The presence of salts also other reactions are influenced. For example, the concentration of furfurals decreases. Figure 2 shows the concentration of Hydroxymethylfurfural, Methylfurfural and Furfural after the conversion of glucose. The addition of potassium salt drastically decreases the yield of furfurals. This is important; because of furfurals have the tendency to polymerize. Polymerisation is an unwanted side reaction of hydrothermal gasification, leading to a reduction of gas yield.

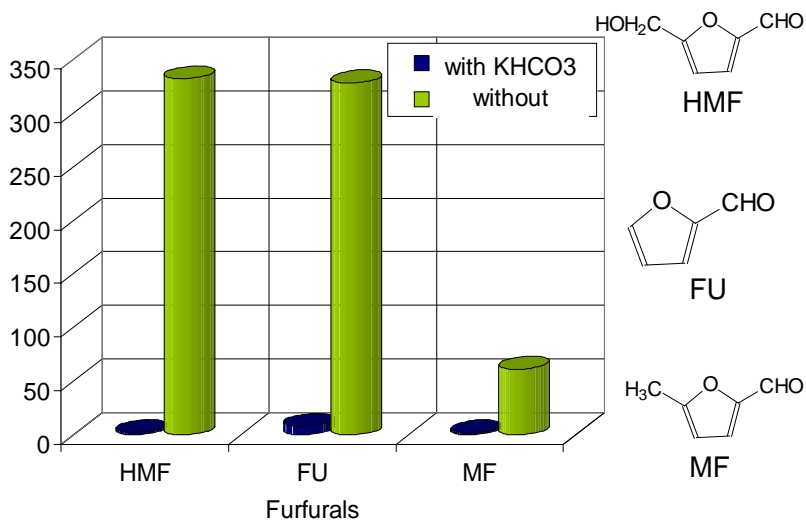


Fig.2: Yield of the furfurals Hydroxymethylfurfural, Methylfurfural and Furfural after Glucose gasification as function of reaction time with and without the addition of  $\text{KHCO}_3$  (1.5 % (g/g) Glucose, 0.2 % (g/g)  $\text{KHCO}_3$ , 25 MPa, 500 °C, tubular reactor)[5].

The basic idea of the new concept introduced here is to use hydrothermal brine as a catcher for salts, which may cause plugging, and as a highly efficient catalyst for gas formation.

### EXPERIMENTAL SET-UP

A salt forming a liquid phase (“hydrothermal brine”), usually a potassium salt, is deposit in the reactor. This liquid phase can be regarded as water containing melt. A model mixture of

glucose and a sodium salt is fed into the reactor continuously. Sodium salts like the one used here deposits as solid and may cause plugging of the reactor [6]. In the semi-continuous set-up as depicted in Fig. 3, they should be absorbed in the hydrothermal brine.

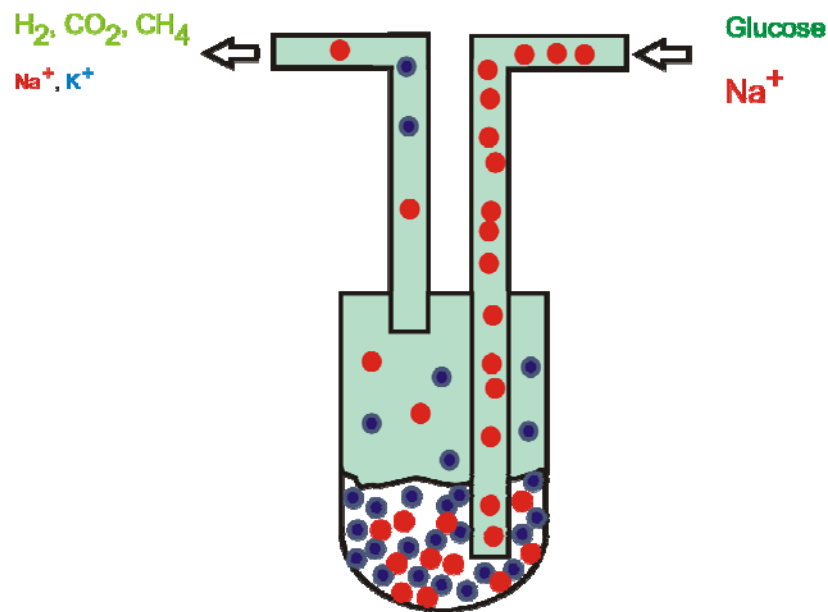


Fig. 3: Schematic set-up of the semi-continuous process investigated.

## RESULTS

Fig. 4 shows the concentration of potassium and sodium ions in the effluent as function of time. In this semi-continuous process, sodium salt is continuously fed into the reactant but the concentration of the effluent is much lower than the input concentration and remains constant. At the time, the feeding of the sodium salt solution starts the potassium salt concentration in the effluent increases. In the moment the sodium salts enters the brine, the potassium ion concentration increases. The decrease of sodium concentration after passing the reactor means that the sodium is captured in the brine. The ratio potassium salt to sodium salt in the hydrothermal brine increased continuously with time. This ratio is also shown in Fig. 4. In additional experiments, glucose was fed continuously into the reactor and into the potassium salt brine. Fig. 5 shows the gas yields for these experiments. Carbon dioxide is always the main gaseous product. At 500 °C, the addition of  $\text{KHCO}_3$  or  $\text{NaHCO}_3$  decreases the yield of hydrogen and carbon monoxide. In the case of  $\text{NaHCO}_3$  addition, the carbon dioxide yield is lower than in the other cases.

At 425 °C, hydrogen and carbon monoxide are nearly identical in all three cases. Here the methane yield is highest in the case of  $\text{KHCO}_3$  addition. In addition, the carbon dioxide yield is higher than without salts and  $\text{NaHCO}_3$  addition.

The brine has a black colour after reaction.

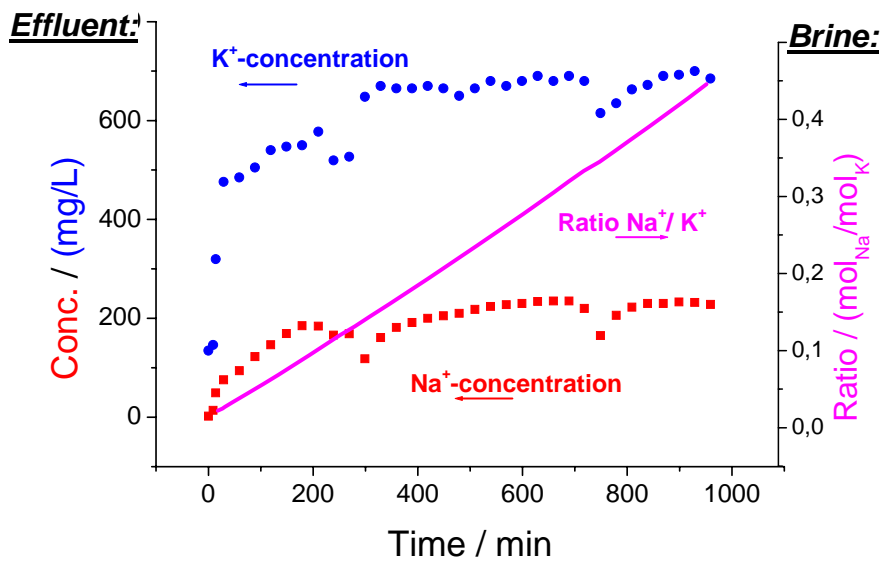


Fig. 4: Brine (425 °C, 28 MPa) of  $\text{KHCO}_3$  was furnished into the reactor before the experiments. Then at the time = 0 minutes a solution of  $\text{NaHCO}_3$  (2 % (g/g)) was fed into the reactor (200 mg/h). The concentrations of  $\text{Na}^+$  and  $\text{K}^+$  in the effluent are given at the left axis. The ratio of  $\text{Na}^+$  to  $\text{K}^+$  in the brine is given at the right axis.

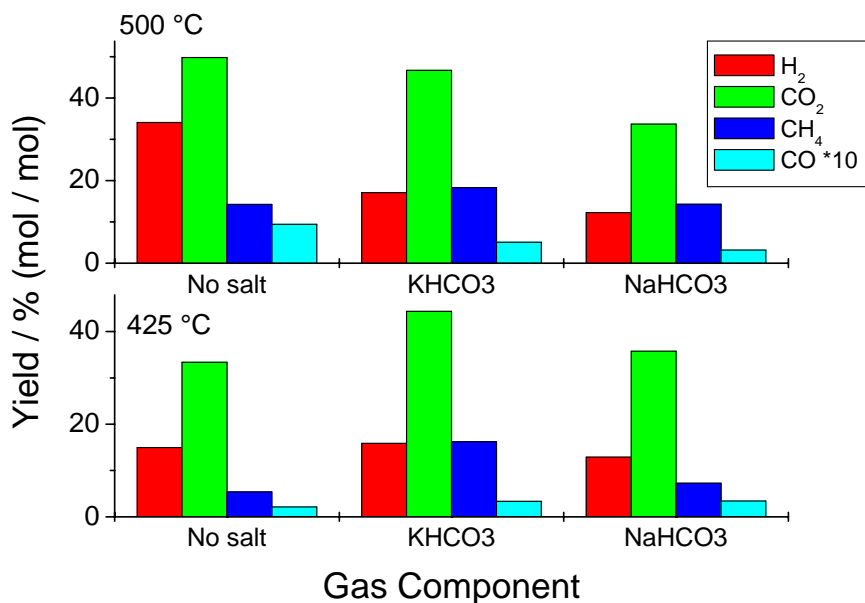
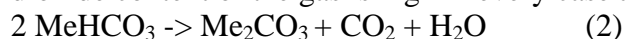


Fig. 5: A brine of  $\text{KHCO}_3$  was furnished into the reactor before the experiment. An aqueous flow (200 mg/h) containing glucose (5 % (g/g)) with and without salt passes through the reactor filled with the brine. The gas yields (mole gas component / mole glucose) for glucose gasification at 500 °C and 425 °C, respectively, are depicted. Investigated were pure glucose solution, an aqueous solution of glucose and  $\text{KHCO}_3$  (2.5 % (g/g)) or of glucose and  $\text{NaHCO}_3$  (1 % (g/g)) always at 28 MPa.

## DISCUSSION

The fact that the sodium concentration remains constant, also when continuously sodium salts solution is fed into the reactor, shows that the hydrothermal brine is an effective catcher for salts. At 425 °C (Fig. 5), the CO yield is low, also in the case when no salts are added. The reason is that the salt forming the brine acts as catalyst for the water-gas shift reaction (equation (1)). In spite of this, the carbon monoxide yield is further decreased by addition of salt in the feed. Likely the reaction partly occurs outside of the brine, e.g. in the inlet of the reactor. It is surprising that the hydrogen yield decreases in the case  $\text{KHCO}_3$  or  $\text{NaHCO}_3$  is added into the feed. This is difficult to explain. Perhaps side reactions consuming hydrogen, e.g. hydrogenation of intermediates or coke precursors, leads to the reduction. The carbon dioxide content of the gas is high in every case as consequence of the following reaction:



Likely, a mixture of  $\text{Na}^+$  and  $\text{K}^+$  carbonates behave different concerning this reaction compared with  $\text{K}^+$  carbonates system, therefore the carbon dioxide content in the gas phase is different. At 500 °C, the addition of salts in the feed does not change the hydrogen and carbon monoxide yield distinctly. Likely, at this temperature, the reactions inside the brine are strongly dominant, and the reactions before entering the brine are for minor importance. At 500 °C, the methane yield is relative high when  $\text{KHCO}_3$  is added in the feed. This is surprising, usually the methane formation needs hydrogenation catalyst like Nickel [7]. Here further investigations are necessary. The also high yield of carbon dioxide may be a consequence of the high input of carbonate and the higher tendency to release carbon dioxide from  $\text{K}^+$  brine than from the  $\text{K}^+/\text{Na}^+$  mixed carbonates.

It has to be considered that in the experimental set-up used, not supercritical water but a melt, called brine here, and is the reaction medium. Reactions of biomass in salt melts are investigated before, but in these cases, the melts are dry [8]. Therefore, there is no knowledge what happens in the hydrothermal brine. The black colour might be a hind that the coke formation is an unwanted side reaction. Usually the coke formation is assumed to be a consequence of furfurals polymerisation [9]. It is also observed that salts might be seeds for polymerisation. On the other hand, as mentioned in the introduction, alkali salts reduces the yield of furfurals and therefore coke formation. This is the case at hydrothermal conditions. At dry conditions salts increases gas and coke formation [10]. The coke formation is enhanced likely by supporting the polymerisation of Anhydroglucose. Furfurals and Anhydroglucose are both intermediates of glucose and cellulose degradation. Anhydroglucose is of higher importance in dry systems than in hydrothermal systems, but the behaviour in a hydrothermal brine is completely unknown. Likely, the brine behaves more like a “dry” system than the low-density phase of supercritical water, usually used as reaction medium for hydrothermal gasification.

## CONCLUSION

The hydrothermal brine is found to be effective as catcher for salts, here a sodium salt, which may cause plugging. The carbon dioxide content in the gas phase after glucose gasification is low due to catalysis of the water-gas shift reaction. Unfortunately, the gas yield decreases when salts are in the feed, not only in the brine. This is a draw back in view of technical realisation. The reason is not clear like the whole chemistry of biomass degradation in a hydrothermal brine. Here further investigations are necessary.

## REFERENCES

- [1] KRUSE, A., *The Journal of Supercritical Fluids*, Vol. 47, **2009**, p. 391
- [2] BAIERLEIN, H., Doctoral thesis, University Erlangen-Nürnberg, **1983**.
- [3] GOLDACKER, H., DAHMEN, N., KRUSE, A., German Patent DE102007002056, **2009**

- [4] KRUSE, A., DINJUS, E., Zeitschrift für Physikalische Chemie. Neue Folge, Vol. 219, **2005**, p. 341
- [5] SINAG, A., KRUSE, A., SCHWARZKOPF V., Engineering in Life Science, Vol. 3, **2003**, p. 469
- [6] KHAN, M. S., ROGAK, S. N., The Journal of Supercritical Fluids, Vol. 30, **2004**, p. 359
- [7] ELLIOTT, D. C., Biofuels, Bioproducts and Biorefining, Vol. 2, **2008**, p. 254
- [8] RAJA, Y., Journal of the Institution of Engineers (India), Part T: Technician's Journal. **1989**, Vol. 70, p.15
- [9] KAAYILDIRIM, T., SINAG, A., KRUSE, A., Chemical Engineering & Technology, Vol. 31, **2008**, p. 1561
- [10] RICHARDS, G. N., ZHENG, G. C., Journal of Analytical and Applied Pyrolysis, Vol. 21, **1991**, p. 133