

# EFFICIENT TAR DEGRADATION USING CHARCOAL

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## Abstract

The use of biomass as a precursor for carbonaceous materials is an old but still very important subject. The basic upgrading process is the pyrolysis process. Beside the initial degradation reactions forming gases, tars (e.g. anhydroglucopyranoses) and primary char the secondary reactions are determining the total char yield. Additionally, secondary reactions of the tars reduce the tar content in the pyrolysis gas. Therefore, these reactions are of special interest to obtain an almost tar free gas. This work focuses on these secondary reactions taking place in the pyrolysing particle, in the gas phase and at pyrolysed particles. Each site of reaction is investigated experimentally and theoretically using the molecular modelling approach to obtain kinetic data. The experimental results show a significant reaction rate of tars at charcoal particles. Hence, charcoal is a promising material for tar degradation. The surface groups of the charcoal are characterised using temperature programmed desorption (TPD) experiments. The tars are collected in 2-propanol as solvent following the tar sampling guideline. Additionally, the molecular weight distribution is measured by size exclusion chromatography using pyridine as solvent. The different sites of reactions lead to characteristic changes in the molecular weight distribution.

## Introduction

In the frame of biomass upgrading to higher value products the carbonisation takes place in almost all thermal processes. Beside a high calorific char and pyrolysis gases, condensables and biomass tars are formed. The latter is reducing possible applications of the gaseous products. In detail, the maximum tar fraction is for gas engines, gas turbines, and fuel cells 5 mg/m<sup>3</sup>, 100 mg/m<sup>3</sup>, 0.1 mg/m<sup>3</sup>, respectively. Therefore, gas cleaning is necessary. A significant tar reduction during the carbonisation process itself is desirable to reduce gas cleaning costs. Additionally, heterogeneous tar degradation is increasing the char yield. Therefore, the knowledge of tar reaction is necessary to increase the char yield.

This work deals with the formation of biomass tars and the degradation at different reaction sites. The intra-particle degradation, homogeneous degradation in the gas phase as well as heterogeneous tar degradation at charcoal samples is investigated.

## Experimental Set-Up

The experimental set-up has been described in (Klose, W. and A.-P. Schinkel 2006). It consists of 2 consecutive electrical heated reactors. The first is carried out as a thermal balance, where the carbonisation of the biomass sample takes place. The nitrogen gas purges the pyrolysis gases, condensables, and tars. In the second tubular reactor homogeneous and heterogeneous tar degradation is investigated at various residence times and temperatures. The formed tars and condensables are collected in 6 impinger bottles using 2-propanol as solvent. The remaining gases are detected by analysers for carbon dioxide, carbon monoxide, methane, and hydrogen.

The mass of the tars is detected gravimetrically by evaporation of the solvent and the condensables, following the guideline for sampling and analysis of tars (Neeft et al. 1999). The molecular weight distribution (MWD) is determined by size exclusion chromatography using pyridine as solvent. The calibration of the detector is carried out by the tar mass fractions of tar samples collected at the outlet of the detector. The molecular weight distribution is determined using additionally the molar fraction of tars in the collected samples. The molar fraction is determined by vapour pressure osmometry.

## Determination of kinetic parameters

To describe the degradation of biomass and the formation of tars, gases, and chars a first order approach is used. Following the transition-state theory the pre-exponential factor is only slightly dependent on the bond scission. For a wave number of 1000 cm<sup>-1</sup> the pre-exponential factor leads to

$$k_0 = 1,884 \cdot 10^{10} \cdot T \frac{1}{K_S}$$

The vibrational partition function is evaluated at a temperature of 340 °C. The biomass and most of the tars have more than 50 vibrational degrees of freedom. Therefore, the energy transfer by collision (Lindemann-Theory) is not considered. As mentioned in (Hase et al. 1989) the activation energy can be calculated by the peak temperature of the different reaction complexes by a pre-selection of the pre-exponential factor. In the field of reaction engineering it is often useful to describe parallel reaction by one reaction to save computational resources. In this case the pre-selection of the pre-exponential factor leads to kinetic parameters being valid over a wide heating-rate range in contrast to the fitting of both kinetic parameters. In this case the fitting of both Arrhenius parameters leads to very small values of the activation energy and the pre-exponential factor. This is illustrated in fig. 1 that shows a reaction rate calculated considering an activation energy distribution, a reaction rate calculated by very small values of the kinetic parameters and a reaction rate calculated by pre-selection of the pre-exponential factor. The curve calculated with the very small values of the kinetic parameters represents the data calculated with an activation energy distribution very good, symbolising the degradation of the lignin fraction of biomass. Fig. 2 and fig. 3 show the results if the heating-rate slows down to 0.005 K/s and 0.002 K/s. The reaction rate calculated with the very small values of the kinetic parameters does not fit the experimental data in total. The pre-selection-approach leads to robust kinetic parameters being valid also for this heating-rate. Based on this approach the kinetic data are determined for biomass degradation and tar degradation.

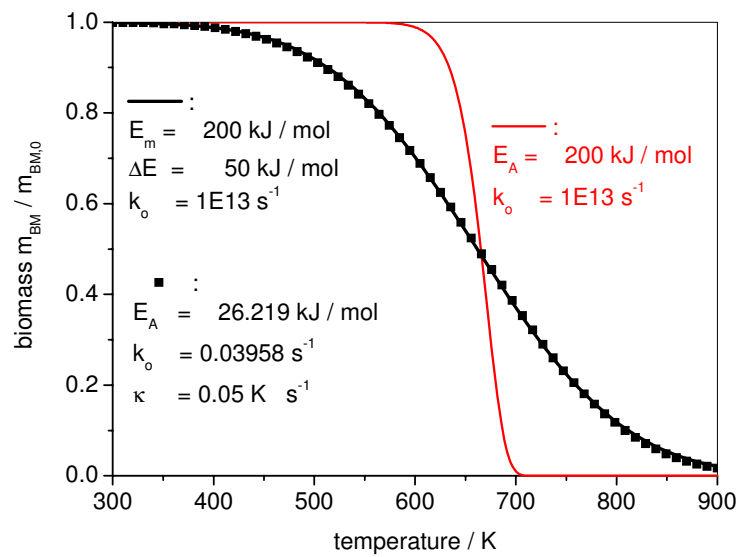


Fig. 1 Mass loss vs. temperature calculated for a heating-rate of  $\kappa = 0.05 \text{ K/s}$  using different reaction approaches

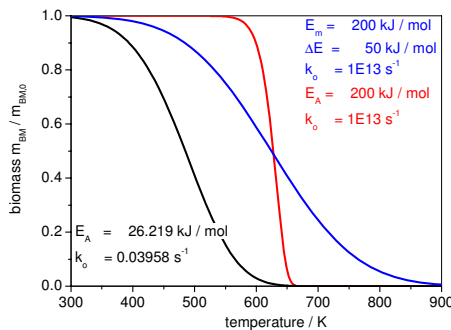


Fig. 2 Mass loss vs. temperature calculated for a heating-rate of  $\kappa = 0.005 \text{ K/s}$  using different reaction approaches

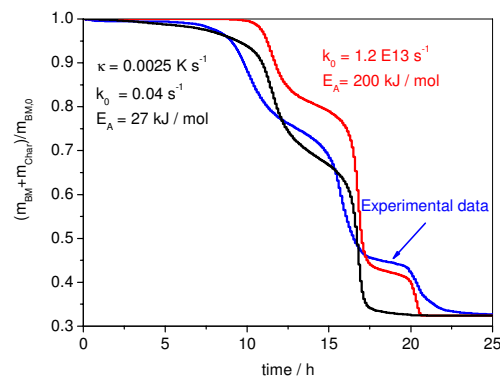


Fig. 3 Mass loss vs. time measured and calculated for a heating-rate of  $\kappa = 0.002 \text{ K/s}$  using different reaction approaches

## Experimental results

### Intraparticle tar degradation

The first step of tar degradation takes place in the carbonising particle. A good indicator is the carbon monoxide signal. The carbon monoxide yield is increasing with increasing particle diameter 1.5 mm, 4 mm, 5.5mm, and 10mm due to secondary tar reactions. The maximum yield on carbon monoxide derived from the hemicellulose reaction complex from beach wood is about 1.2 %. The degradation of tars formed by the lignin complex forms methane and increases the solid yield. The increase of carbon yield due to the degradation of tars formed by the cellulose reaction is of minor importance.

The following assumptions are made to describe the heterogeneous intra-particle tar degradation:

- the degradation of each reaction complex is assumed to be pseudo stationary,
- the reaction is isothermal for each reaction complex
- the formation of tars are assumed to be constant over a time interval
- the flow is assumed to be laminar parabolic velocity field following the Hagen-Poiseuille's velocity distribution

Therefore, one can obtain from the mass balance

$$w(r) = \frac{k_1 x}{P(x)}$$

The momentum balance leads to

$$\frac{dP(x)}{dx} = -k_2 x$$

Introducing the Langmuir-Hinshelwood-concept the total yield can be expressed by

$$\alpha = \frac{1}{L} \int_{r_1}^{r_2} \int_0^L \frac{k_3 (k_4 (L^2 - x^2) + P_v)}{1 + k_5 (k_4 (L^2 - x^2) + P_v)} dx dt$$

This leads to

$$\alpha = \alpha_{\infty} - \frac{A \operatorname{Arctanh}\left(\frac{L}{\sqrt{B + L^2}}\right)}{\sqrt{B + L^2} L}$$

Figure 4 shows the experimental data and the model results of carbon monoxide formation due to heterogeneous tar degradation of the hemicellulose reaction complex.

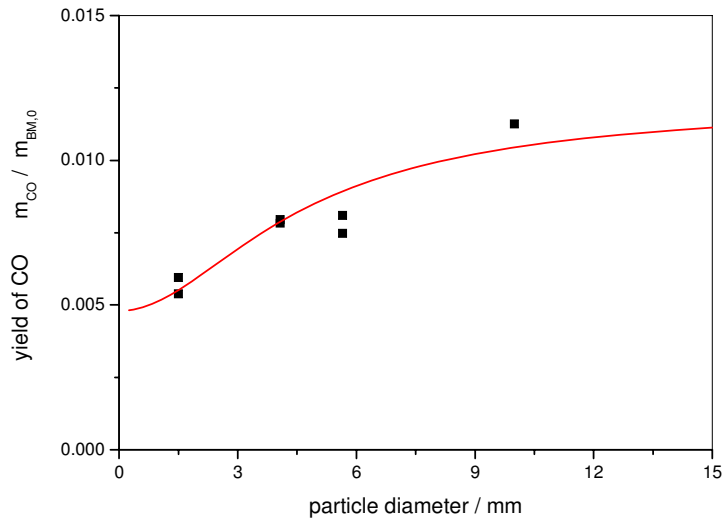


Fig. 4 Intra-particle carbon monoxide formation due to tar degradation formed from the hemicellulose reaction complex

The changes of the tar due to degradation reactions at different reaction sites is characterised by molecular weight distribution. Fig.5 shows the molecular weight distribution (MWD) of tars derived from beech wood. The red curve is the MWD of a tar derived from 1.5 mm beech wood particles. The external particle surface area is  $A = 0.007 \text{ m}^2$ . The black curve represents the MWD from tars derived from larger particles diameter while keeping the external surface area constant. Hence, the changes can be identified by intra-particle reactions. Tar

compounds are reduced over the whole range of the MWD. The lower region of the MWD is reduced by keeping the particle diameter constant and increasing the external surface area of the sample.

Fig.6 shows the influence of homogeneous tar degradation at 600 °C. The main peak is shifted to lower MW. A significant reduction of tars can be observed. Additionally, a reduction of the tar content can be achieved by introducing charcoal. Fig.6 shows the MWD for two residence times in the secondary reactor. In fig.7 one sees the reduction of tars vs. the residence time at 600°C and 800 °C for homogeneous and heterogeneous tar degradation.

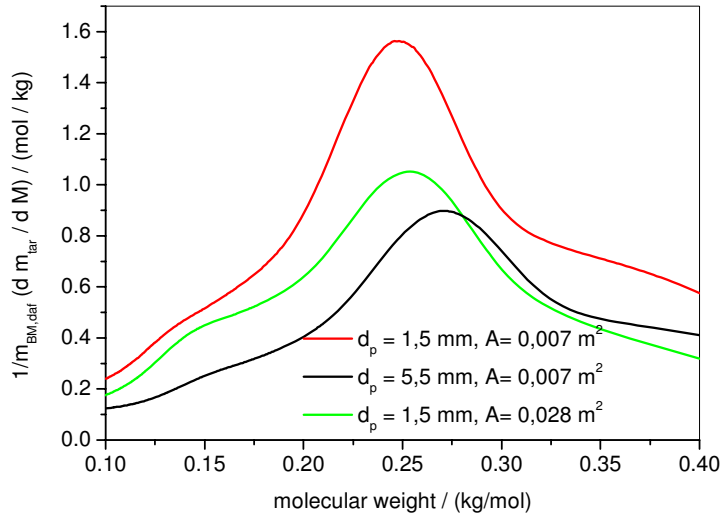


Fig. 5 Molecular weight distribution of tars effected by intra-particle and outer-surface degradation

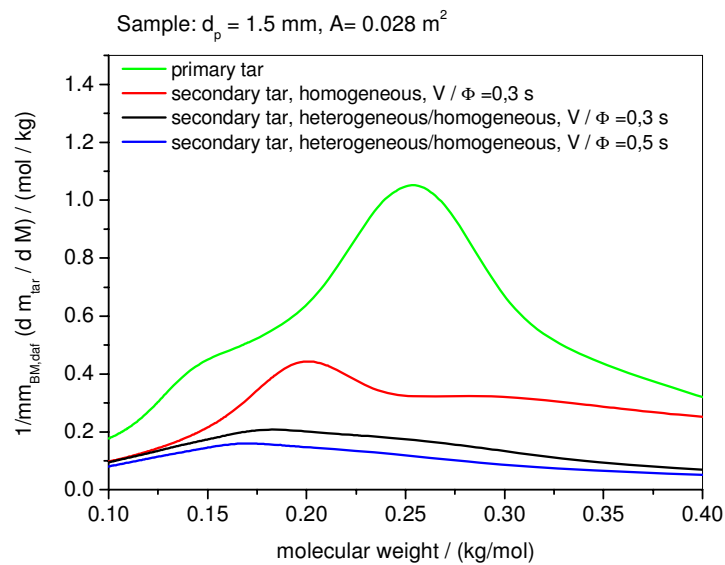


Fig. 6 Molecular weight distribution of secondary tars effected by homogeneous and heterogeneous/homogeneous tar degradation

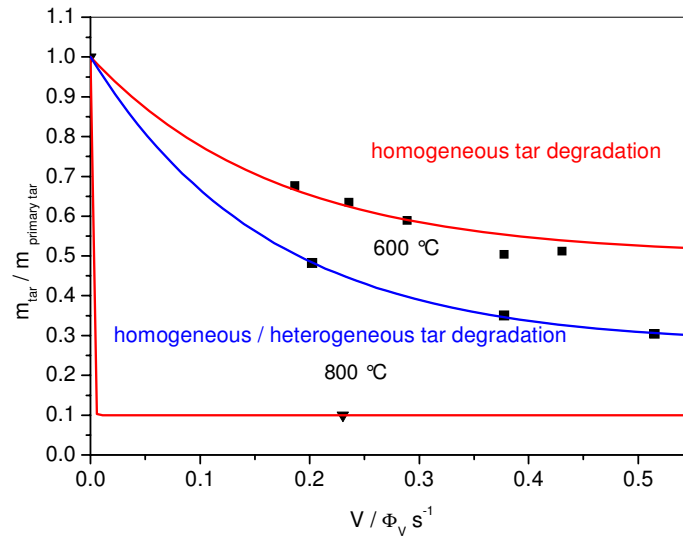


Fig. 7 Tar degradation due to homogeneous and heterogeneous/homogeneous tar degradation

## Conclusion

Tar degradation has been studied at different reaction sites. In detail intra-particle reactions, heterogeneous reactions at the pyrolysing particle surface area as well as homogeneous tar degradation reactions and heterogeneous tar degradation at pyrolysed particles has been investigated. The first step is the intra-particle tar degradation, the second is the homogeneous and heterogeneous tar degradation. At a temperature of 600 °C the tar content can be reduced over 50 %. The tar content is reduced additionally over 40% by introducing charcoal into the secondary reactor. Therefore, the carbon yield can be increased and the tar yield decreases significantly by intra-particle reactions due to increasing particle diameter. This effect is limited. Hence, the variation of particle diameters is effective only up to a characteristic particle diameter. This particle diameter depends on the pore structure of the particles, i.e. partial pressure of the tar, and on the amount active surface sites.

## References

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