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Benzene steam reforming kinetics in biomass gasification gas cleaning

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HIGHLIGHTS

- Effect of gasification product compounds on steam reforming of benzene was studied.
- H_2 decelerate and CO_2 accelerate the reforming kinetics.
- The acceleration by CO_2 could not be explained only by simultaneous dry reforming.
- Langmuir-Hinshelwood model described air gasification gas reasonably well.

ARTICLE INFO

ABSTRACT

Benzene steam reforming kinetics was studied in conditions relevant to biomass gasification gas cleaning on Ni/Al_2O_3 catalyst i.e. temperature range 750–900 °C and in presence of H_2S. The benzene concentration was 600–3500 ppm. The qualitative effect of the main gasification product gas compounds on the benzene steam reforming kinetics was studied. The first order kinetic model in respect to benzene was used to compare the effect of H_2, CO and CO_2. It was observed that especially H_2 decelerated and CO_2 accelerated the benzene steam reforming kinetics. With a gas mixture representing air gasification gas, the Langmuir-Hinshelwood type model taking account effect of H_2 in denominator described the benzene decomposition well. However, the model did not describe the kinetics of benzene steam reforming for the gas representing O_2/H_2O gasification gas.

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1. Introduction

Thermochemical conversion of biomass by gasification is one route to produce renewable fuels and chemicals. The gas produced by biomass gasification contains impurities that need to be cleaned before the gas can be utilized for fuel production. The hydrocarbon impurities (light hydrocarbons and tar) in the gasification gas can be converted into syngas by steam reforming. In addition to hydrocarbon impurities, the gas contains, among others, H_2S which is a known catalyst poison. The H_2S content in the gasification gas produced from forest residues is typically around 40–120 ppm [1].

Kinetics of tar decomposition in biomass gasification conditions have been studied with many catalysts such as dolomite, olivine, steam reforming type nickel catalysts and precious metal catalysts [2]. The dolomite and olivine catalysts are not as active as nickel or precious metal catalysts. They are more typically used in-situ as gasifier bed materials to reduce the tar concentration in the outlet gas than as a secondary bed to completely purify gasification gas

from tar compounds, whereas nickel and precious metal catalysts are used in the secondary reformer.

In kinetic studies, tar is typically studied by combining tar compounds to one or several lumps or by using tar model compounds. Furthermore, the first order kinetics is typically assumed towards tar or tar model compounds. Palma [2] has collected in a review article kinetic parameters from different studies using model compounds or real gasification gas. In the studies with real gasification gas, the gas composition and conditions cannot be varied as freely as in the laboratory scale experiments and the effect of different compounds on kinetics cannot be studied so easily. On the other hand, most of the laboratory studies with model compounds have been conducted without H_2S. The conditions for the kinetic studies has to be carefully chosen since steam reforming is a fast, strongly endothermic reaction leading easily to mass transfer limitations and temperature gradients in the catalyst bed. The effectiveness factor is low in industrial scale reactors [3].

Considering studies of individual tar components, Jess [4] has studied steam reforming kinetics of various aromatic compounds, including benzene, with simulated coke oven gas with Ni/MgO catalyst. The gas mixture studied with contained 0.2 vol% of benzene,

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H_2 30 vol% and H_2O 13 vol% in nitrogen at 410–800 °C. No H_2S was used in the experiments. For benzene reforming, first order kinetics was assumed. The pre-exponential factor was $2 * 10^{11}$ m^3 s^{-1} kg^{-1} and the activation energy 196 kJ/mol.

Swierczynski et al. [5], in turn, have studied toluene steam reforming with Ni/olivine catalyst. The gas mixture used in the experiments contained toluene 4709 ppm, 7.5% H_2O and Argon to balance. H_2S was not included in this study either. They assumed as well the first order kinetics for toluene steam reforming and the pre-exponential factor was $3.14 * 10^{13}$ m^3 kg_{cat}^{-1} h^{-1} and the activation energy was exactly the same as in the study of Jess [4] for benzene, 196 kJ/mol. Carbon monoxide was the primary reaction product but with higher space times, also CO_2 was formed via water gas shift reaction.

Devi et al. [6] have studied steam and dry reforming of naphthalene on olivine without H_2S in the gas. They studied the effect of gas compounds on naphthalene conversion at 900 °C. Similar naphthalene conversion was obtained at steam and dry reforming modes. However, with gasification gas (air gasification type composition), the conversion was lower because the conversion was decreased by the presence of hydrogen. They used power law model for naphthalene steam reforming. The reaction order for naphthalene was 2.04, for H_2 −0.74, CO 0.2, CO_2 0.94 and H_2O 1.79.

Simell et al. have studied both steam [7] and dry reforming [8] kinetics of benzene on dolomite catalyst. The steam reforming kinetics of benzene could be described by Langmuir-Hinshelwood mechanism. In the conditions of the study, steam did not have an effect on reaction rate but H_2 decreased the reaction rate. The rate determining step in the model was single site adsorption of benzene on the catalyst.

Corella et al. [9] have studied steam reforming kinetics of tar in real gasification gas from an air gasifier. They divided the tar compounds in different lumps and modelled the rate of reforming for the tar lumps. As a catalyst they used nickel catalyst with particle size of 7–14 mm. The kinetics were likely limited by mass transfer since in their earlier, study they used smaller particle size of the same catalyst and reported with that particle size that the kinetics were controlled by internal diffusion [10].

In this study, the qualitative effect of main gasification gas compounds on steam reforming kinetics of benzene was studied in presence of H_2S on nickel catalyst. The temperature range 750–900 °C was chosen to cover the practical reformer temperatures, which are required to avoid the complete deactivation of the catalyst by H_2S [11]. Benzene was chosen as a model compound because it is thermally very stable aromatic compound [12]. Consequently, the reformer design could be based on steam reforming

rate data of benzene in cases where only tar reforming is necessary. An example is a biomass gasification plant producing only SNG, where low methane conversion in the reforming is an advantage.

2. Experimental

2.1. Laboratory experiments

The experiments were carried out in an atmospheric plug flow reactor system described in [13]. The reactor was a quartz tube of 10 mm inner diameter with 4 mm thermocouple pocket in the centre of the reactor. The reactor was placed in a three zone furnace. The catalyst was placed on a quartz sinter. The gases were fed by mass flow controllers from the gas cylinders. The gas compositions used in the experiments are presented in Table 1. The gasification gas 1 represented the product gas of air gasifier. The gasification gas 2 represented the gas from steam-oxygen blown gasifier; however the H_2O concentration was kept the same as in gasification gas 1. The gases were supplied by Aga and their purities were as follows: CO 99.97%, CO_2 99.99%, H_2 99.999%, CH_4 99.995%, N_2 99.999, H_2S 0.500 mol% in N_2. Benzene (Merck, >99.7%) and water (ion exchanged) were fed by HPLC pumps. Benzene was fed to the heated line with other gas components, whereas water was fed through a vaporizer before mixing it to the gases. The H_2S concentration of 100 ppm in dry gas was chosen based on typical concentration in the biomass gasification gas and it was kept constant in all the experiments.

Benzene and other hydrocarbons were analysed by GC/FID (Agilent 7890A). In some of the experiments with gas mixtures of Bz + H_2O and Bz + H_2O + H_2, the permanent gases (H_2, CO, CO_2, N_2) and H_2O were analysed by GC/TCD (Agilent 6850) to examine the

Table 1
Gas compositions in the experiments, the gas mixtures contained N_2 for balance.

	Dry gas				Wet gas	
	CO (vol%)	CO_2 (vol%)	H_2 (vol%)	H_2S (ppm)	H_2O (vol%)	C_6H_6 (ppm)
Bz + H_2O	0	0	0	100	10	600–3500
	0	0	0	100	4.25–12.76	3500
Bz + CO_2	0	14.9	0	100	0	3500
Bz + H_2O + CO	12.5	0	0	100	10	3500
Bz + H_2O + CO_2	0	15	0	100	10	3500
Bz + H_2O + H_2	0	0	11	100	10	3500
Gasification gas 1	12.5	15	11	100	10	3500
Gasification gas 2	25	20	35	100	10	3500