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Steam reforming of methane in a synthesis gas from biomass gasification

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ABSTRACT

An experimental and modeling study of the pyrolysis and of the steam reforming of methane in mixtures representative of a gas produced from biomass gasification has been performed. The experimental study has been done in a plug flow reactor under a near atmospheric pressure (1.07 bar), for a residence time of 0.68 s and temperature ranging from 1200 up to 1800 K. Reactants and products were quantified on-line at the exit of the reactor by gas chromatography. The kinetic influence of the different gases present in the synthesis gas (H_2O , H_2 , CO , CO_2) on the methane conversion has been investigated. Water steam has shown a very limited impact on conversion, even at the highest temperature, while hydrogen exhibited a strong inhibiting effect on the reforming reaction. Carbon dioxide promoted slightly the reaction, unlike carbon monoxide, which had no kinetic effect. A temperature as high as 1700 K is necessary in these conditions to convert entirely methane. A model derived from that for the combustion of light hydrocarbons was developed with attention to the reactions of unsaturated species with hydroxyl radical OH, which are responsible for the reforming. The main experimental trends are well reproduced. Carbon reforming occurs mainly by reactions of OH radicals with unsaturated C_2 molecules, which are soot precursors. Process conditions necessary for high temperature methane reforming would then be favorable to undesirable soot formation.

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Introduction

Environmental concerns, especially greenhouse gases emissions, have led to an increased interest in the use of renewable energies. Biomass is widely used in combustion but can also be involved in more advanced applications such as the production of liquid combustibles (GTL) or the cogeneration by means of a fuel cell [1]. These applications require the production of a high quality synthesis gas (syngas, mixture of CO and H_2). Cellulosic biomass may be a promising feedstock

through the gasification processes [2,3]. Wood gasification is a heterogeneous process between a carbon-containing solid and an oxidizer such as O_2 , CO_2 or water steam [4,5]. The main products are CO and H_2 , but large fractions of hydrocarbons, char and soot, which are undesirable to achieve a high efficiency and avoid fouling, are yielded too. Three phases can be distinguished [6]. The solid phase includes soot and char. The liquid phase involves the condensable intermediates named as tars, while carbon oxides, hydrogen, water, methane and other light hydrocarbons remain in the gas phase. The hot gases from the gasification need to be cleaned drastically to

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reach the severe specifications of fuel cells or catalytic processes [7]. Catalytic post treatment are usually used to clean the gases at the exhaust of the gasification [8], but the severe conditions, especially the high temperature, lead to a short life time for the catalytic bed. A non catalytic alternative can be a high temperature steam gasification and reforming of a mixture of biomass and methane, which permits to optimize hydrogen yields for downstream liquid fuel synthesis and shows a rather good efficiency over autothermal process [9,10]. Another alternative process would be a homogeneous high temperature reforming of tars ($T > 1273$ K) and light hydrocarbons at the exhaust of the gasifier. This would allow a cleaning of the gas and an improvement of the global yield by oxidizing the remaining hydrocarbons into CO and H_2 [11]. The technical evaluation of such an alternative is required to know precisely the kinetics of the hydro reforming of hydrocarbons. These reactions are also involved in other processes proposed for the production of hydrogen, such as solar driven methane [12] or carbonaceous material steam reforming [13,14] or auto-thermal reforming using partial oxidation of hydrocarbons [15–18]. Up to now, modeling of gas phase reforming or water gas shift reaction in thermal processes often relies on thermochemical equilibrium [19] or global stoichiometric equations [20].

Few studies have been devoted to the reaction of hydrocarbons and tars with water steam. Jönsson [21] studied the conversion of methane in a gas obtained from wood pyrolysis, in a tubular reactor. The conversion was found to be maximum at 1523 K (60% conversion) and to be not very sensitive to the amounts of water and oxygen, while hydrogen showed an inhibiting effect. Tijmensen [22] studied the reaction of methane with water between 973 and 1373 K between 10 and 35 bar and proposed a global reaction rate. Valin et al. [23] followed the conversion of methane in a pilot scale tubular reactor in a gas mixture representative of that obtained after the gasification of wood. 90% of the hydrocarbon was oxidized at 1653 K for a residence time of 2s and they noted also the inhibiting effect of hydrogen [24].

Reactions of tars have been also the subject of some studies. At high temperature, tars are mostly composed of aromatic and polyaromatic compounds [6]. The major components are benzene, toluene, indene, naphthalene, and phenol [25]. These compounds could then be used as surrogates for the reactions of tars. Jess [26] studied the steam reforming of benzene, toluene, and naphthalene in a tubular reactor between 973 K and 1673 K under 1.6 bar. Toluene was found to be completely consumed at 1300 K while a temperature of 1700 K was necessary to convert benzene.

Although many detailed kinetic models exist for the thermal decomposition and the combustion of light hydrocarbons, especially for methane [27–37], these models were not designed to simulate the slow oxidation by water in a reducing atmosphere containing mainly CO and H_2 . Reactions at very high temperature in a mixture rich in H_2O , CO, CO_2 and H_2 need further investigations. The present work aimed to go further than the process study by Valin et al. [23] and to investigate the kinetic behavior and interactions of the different compounds in well-defined conditions. An experimental and modeling study of the thermal cracking of methane has been performed at high temperature in a

synthetic gas representative of that produced by the gasification of biomass. The effect of temperature and composition has been investigated and is discussed.

Experiments

The experimental study has been performed in a continuous flow reactor under a near atmospheric pressure (800 Torr, 1.07 bar). The reactor was a tubular mullite pipe (60 cm length and 2.4 cm internal diameter) of internal volume 271 cm^3 involving a S/V ratio of 1.67 cm^{-1} . The mullite, which is an oxide of silicon and aluminum, allows a heating up to 1900 K. Comparisons were made at lower temperature, between 973 and 1273 K, with a fused silica reactor to check that no wall reaction occurs. Results were found identical in the case of the pyrolysis of ethane up to 1273 K. As pyrolytic carbon deposits were formed in the hottest part of the reactor, the effect of reactor aging was checked in another set of experiments. For a fixed temperature, thermal decomposition of methane, ethylene and acetylene was performed in neat and in coked reactors. It appeared that the formation of carbon deposit had a little promoting influence on the consumption of acetylene, without affecting the conversion of methane and other C_2 hydrocarbons. Experiments were then performed in all cases in clean reactors. A horizontal Vecstar oven allowed heating the reactor up to 1870 K. Temperature profiles were measured by a type S thermocouple coated in an alumina pipe. Uncertainty is estimated to ± 20 K. Fig. 1 presents temperature profiles. A plateau of 16 cm length was reached at the set point temperature but lower temperature regions cannot be neglected in modeling. The reactor can be considered as a plug flow reactor in the studied conditions between 1000 K and 1800 K. For a residence time of 0.68 s calculated in the 16 cm long hot section of the reactor, the Péclet number lies between 120 and 140 as a function of the temperature, whereas a value above 50 allows to consider the reactor as a plug flow reactor.

Messer and Air Liquide supplied gases, with a purity at least above 99.9%. Water was added through a Bronkhorst liquid mass flow controller coupled with a controlled evaporator mixer from the same supplier. For all the experiments, residence time was fixed to 0.68 s (in the hot area), pressure was 800 Torr (1.07 bar) and argon was used as diluent in order

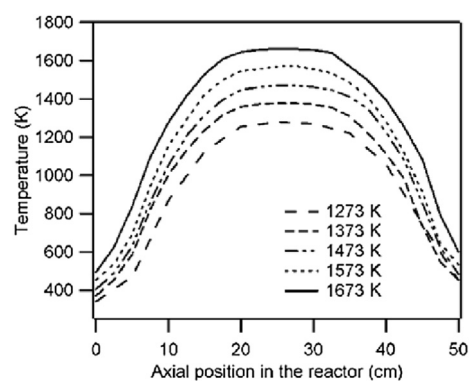


Fig. 1 – Temperature profiles in the reactor as a function of the oven set point.

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