



## Full Length Article

## Interactions between char and tar during the steam gasification in a fluidized bed reactor



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## ABSTRACT

The aim of the present work is to understand the different interactions which may occur between the char and tar model (toluene) in a fluidized bed reactor during biomass char gasification with steam. Experiments are conducted at 850 °C and atmospheric pressure with sand particles as solid medium. The influence of steam and toluene partial pressures on both the char reactivity and the presence of tar in the product gas was investigated in the range of 0.05–0.4 bars and 0.0025 and 0.0075 bars (10.1 and 30.4 g.Nm<sup>-3</sup>), respectively. Results showed that the presence of char in the fluidized bed reactor leads to toluene polymerization (cokefaction) which produces a carbonaceous deposit (coke) on its surface. This deposit is much less reactive towards steam gasification than the initial char. For the operating conditions used in this study, it was found that the rate of tars polymerization ( $R_p$ ) is always smaller than the one of coke and char gasification ( $R_{gr} + R_g$ ). Finally, a comparison between the different solid catalysts in the fluidized bed reactor revealed that olivine is the best catalyst towards toluene conversion when the ratio  $P_{H_2}/P_{H_2O}$  is higher than 1.5 in the reactive gas atmosphere. Otherwise, for a steam partial pressure higher than 0.2 bars, “olivine + 3% char” and “sand + 3% char” were found to be the best compromise to limit the amount of tar in the product gas.

## 1. Introduction

Gasification is a promising way of converting biomass or waste into syngas which can be used for different applications such as catalytic hydrocarbon synthesis and electricity or heat production. However, one of the main problems which hinders the industrial development of gasification processes is the high tar content in the produced syngas [1]. Several approaches for tars removal can be found in the literature and are classified into two types: tars treatment inside the gasifier itself (primary methods) or gas cleaning outside the gasifier (secondary methods) [2]. Tars removal by secondary methods have been widely investigated and are well-established in the literature [1,2]. Primary treatments may have the advantages in eliminating the use of downstream cleanup processes and depend on the operating conditions, the type of bed particles and the reactor design. Therefore, in order to limit the tars concentration in the produced syngas, it is essential to understand the influence of the different solids in the reactor and the reactive gas atmosphere.

Various catalysts were investigated in biomass gasification for tars conversion and have been discussed in several reviews [2–5]. Among them, calcined dolomite and olivine as well as Ni-based catalysts were found to have a strong catalytic activity.

Dolomite is a natural, inexpensive and disposable material. A general agreement is drawn in the literature on the significant effect of dolomite as tars removal catalyst [6–9]. This solid showed a large catalytic activity after calcination at high temperatures which leads to the decomposition of the carbonate mineral to form MgO-CaO. However, this solid is not appropriate in fluidized bed reactors due to its low attrition resistance.

Olivine is another natural, inexpensive and disposable mineral with a global formula  $(Mg_xFe_{1-x})_2SiO_4$ . The main advantage of this material is its strong mechanical resistance which enables its direct use in a fluidized bed reactor (i.e. primary methods) [3]. The use of olivine as tars removal catalyst has been discussed in several studies [8,10–15,18–20]. Its catalytic activity is related to the presence of segregated iron on its surface which may have different oxidation states (i.e. iron(III), iron(II) and native iron). Besides, it was found that iron is more active towards tars removal when its oxidation state is low [7,16,17]. In a previous work on toluene conversion in a fluidized bed reactor [18], it was shown that the reactive gas atmosphere (i.e. oxidizing or reducing) is a key parameter for the catalytic activity of olivine. In particular, the ratio  $P_{H_2}/P_{H_2O}$  controls the oxidation/reduction of iron on the olivine surface. Hence, it was concluded that the catalytic mechanism of tars conversion over olivine can be divided into four

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### Nomenclature

$n_{c, char}^{in}$	amount of carbon in the introduced char (mol)
$\dot{n}_{c, gasi}(t)$	carbon-containing gases molar flow rate at the reactor outlet ( $\text{mol}\cdot\text{s}^{-1}$ )
$\dot{n}_{c, gas+tol}(t)$	carbon-containing gases molar flow rate at the reactor outlet ( $\text{mol}\cdot\text{s}^{-1}$ )
$\dot{n}_{C_7H_8}^{in}$	toluene molar flow rate at the entrance of the reactor ( $\text{mol}\cdot\text{s}^{-1}$ )
$\dot{n}_i(t)$	instantaneous total molar flow rate ( $\text{mol}\cdot\text{s}^{-1}$ )
$\dot{n}_i(t)$	instantaneous partial molar flow rate of component $i$ ( $\text{mol}\cdot\text{s}^{-1}$ )
$\bar{n}_{c, gasi}$	normalized cumulative amount of carbon-containing gases

	at time $t$ (–)
$\bar{n}_{c, gas+tol}$	normalized cumulative amount of carbon-containing gases at time $t$ (–)
$R_c, R_g, R_p, R_{sr}$	rates of coke deposition, char gasification, tars polymerization and coke gasification, respectively ( $\text{mol}\cdot\text{s}^{-1}\cdot\text{mol}^{-1}$ )
$R_T$	normalized rate of carbon-containing tars (–)
$S_{C_6H_6}$	selectivity of benzene (–)
$t$	time (s)
$x_i(t)$	instantaneous molar fraction of component $i$ (–)
$X_c$	carbon conversion rate (–)
$X_{\text{toluene}}$	toluene conversion rate (–)

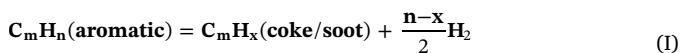
steps (Fig. 1):

- (1) A reduction step: In reducing atmosphere ( $\text{H}_2$  or  $\text{CO}$ ), the iron on the olivine surface is reduced to form reduced iron active sites ( $\text{Fe}^0$ ).
- (2) Polymerization/cokefaction step: These reduced iron active sites catalyze the reaction of tars polymerization (tars cokefaction) to produce a carbonaceous solid deposit on the olivine surface.
- (3) Steam reforming step: This solid deposit is then further converted by gasification reactions.
- (4) Oxidation step: In the presence of oxidizing atmosphere,  $\text{Fe}^0$  is oxidized to give iron with different oxidation states.

Ni-based catalysts also showed a strong catalytic effect in tars removal [21,22]. However, this material has three major limitations: the fast deactivation due to carbon deposition on the solid surface, sulfur poisoning and its lower resistance to attrition in fluidized bed reactors compared to olivine.

More recently, several studies demonstrated that biomass char may have a catalytic effect for tars removal [3,23–31]. The use of char for decomposing tars has some advantages over traditional catalysts. First, the char is a natural and cheap solid product coming from the biomass pyrolysis. Besides, if deactivated it can be easily gasified or burned. Therefore, there is no need of regeneration. Finally, it may be used for tars treatments in both primary (inside the gasifier) and secondary (after the gasifier) methods.

A mechanism for tars conversion over carbonaceous surface was proposed by Fuentes-Cano [23]. The main interactions between tars and char are summarized in Fig. 2. First, the tar compounds meet a fresh char containing a certain number of active sites distributed over the surface. The tar is adsorbed on the char structure and undergoes polymerization or dehydrogenation reactions to form hydrogen and coke (soot). This reaction takes place on the char active sites and can be described by the following expression [24]:



The produced coke/soot stays over the char as a solid carbonaceous deposit. In the following, the rate of Reaction (I) is defined as  $R_p$ .

Overall, the catalytic activity of char is related to its physicochemical properties such as the pores size and surface area as well as the presence of ash or mineral compounds [26].

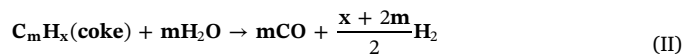
The biomass char properties are not fixed and depend on the biomass type and process conditions. In a previous work [32], it was shown that the pyrolysis operating conditions such as the heating rate, the pyrolysis temperature and the biomass nature strongly influence the hydrogen, oxygen, carbon and ash content in the char as well as the presence of amorphous and aromatic carbons. Hence, it was concluded that both a decrease in the heating rate and a raise of the final pyrolysis temperature lead to an increase in the carbon content and the aromatic structure of char. Besides, some authors [30] found that the char

surface area increases with pyrolysis temperature.

Hosokai et al. [24,28] observed that the specific surface area and the micropores volume ( $< 2 \text{ nm}$ ) decrease during the reforming of tars over char. They concluded that tar compounds are converted to coke (soot) in the micropores. Therefore, the char activity towards tars conversion is maintained by generating micropores during the steam gasification. However, in the case of methane decomposition over char, several researchers [30,33] mentioned that a pores size less than  $1 \text{ nm}$  may lead to diffusion limitations and lower the char activity performance. The presence of ash in the char matrix depends on the type of parent fuels. It was reported that the alkaline and alkaline-earth metallic (AAEM) species in the char mainly influence the rates of coke/soot gasification [25,28].

Besides, bibliographic works [24,26] reported that the larger the number of aromatic rings in the tars, the larger is the tendency for coke formation. For instance, Hosokai et al. [24] observed that phenanthrene and pyrene are more reactive with the charcoal surface than naphthalene and benzene. Therefore, they concluded that heavy tars decomposed faster than light tars.

Fig. 2 also shows that the presence of steam in the reactor leads to the gasification of both the carbonaceous deposit and the initial char according to the following reactions:



In Reaction (III), the char is considered as pure carbon. The rates of both Reactions (II) and (III) are  $R_{sr}$  and  $R_g$ , respectively.

Therefore, two scenarios may be observed in Fig. 2:

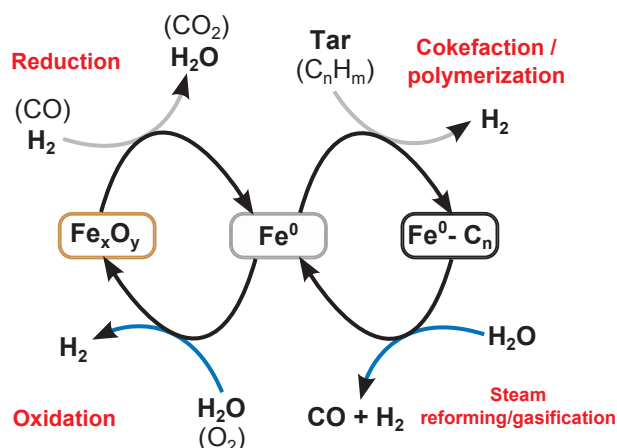


Fig. 1. Schematic diagram of the catalytic mechanism of olivine towards tars conversion [18].

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