



Full Length Article

Tar conversion over olivine and sand in a fluidized bed reactor using toluene as model compound



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ABSTRACT

The aim of this work is to study the tars conversion in conditions representative of biomass gasification in a fluidized bed reactor. Experiments are conducted at 850 °C and atmospheric pressure in a fluidized bed reactor with toluene as tar model. Influences of the nature of the media (sand and olivine) and of the reactive atmosphere (steam and hydrogen partial pressures) on toluene conversion are particularly studied. The steam and hydrogen partial pressures were varied in the range of 0.05 to 0.4 bars and 0 to 0.2 bars, respectively. Results showed a strong influence of these parameters on toluene conversion. Olivine was found to have a catalytic activity towards steam reforming reactions which depends on the ratio P_{H_2}/P_{H_2O} in the reactor. Both thermodynamic equilibrium and surface analyses (EDX and XRD) of olivine particles suggested that this ratio controls the oxidation/reduction of iron at the olivine surface. Besides, iron is more active towards tars removal when its oxidation state is low. At 850 °C and $P_{H_2}/P_{H_2O} > 1.5$, the iron is reduced to form native iron (Fe^0) on the olivine surface which favors the steam reforming of toluene.

1. Introduction

Biomass gasification is considered as a promising alternative route to replace fossil energy for the production of syngas. It is a thermochemical conversion occurring at high temperatures with many simultaneous reactions. Fig. 1 presents a simplified diagram which describes the biomass transformations in successive steps according to the temperature and the reactive atmosphere.

- (i) For temperatures above 350 °C, biomass undergoes a fast thermal conversion. This pyrolysis step converts the biomass into volatile products, either condensable (steam and primary tars) or non-condensable (H_2 , CO , CO_2 , CH_4 and C_2H_x) and a solid residue called char [1].
- (ii) For temperatures greater than 700 °C, the gasification step converts the char into synthesis gas by reaction with steam and carbon dioxide.
- (iii) Milne and Evans [2] suggested that tars from biomass pyrolysis can be classified as primary, secondary and tertiary tars according to the reactor temperature. Primary tars are a mixture of oxygenated compounds coming from cellulose, hemicellulose and lignin conversions. The decomposition of cellulose and hemicellulose mainly leads to the formation of levoglucosan, hydroxyaldehydes and furfurals while methoxyphenols are mostly produced from the

conversion of lignin. Above 500 °C, primary tars are converted into secondary tars which are characterized by phenolic and olefin compounds. Finally, for temperatures above 750 °C, the primary tars are completely destroyed and the tertiary tars appear. They include methyl derivatives of aromatics and Polycyclic Aromatic Hydrocarbon (PAH) series without substituents.

The reactive system of biomass conversion (i.e. pyrolysis and gasification) is an endothermic process. A contribution of energy is necessary in order to maintain the temperature and the different reactions in the reactor. One of the most promising technologies for biomass gasification at large-scale is dual fluidized bed (Fast Internally Circulating Fluidized Bed, FICFB). It consists of two interconnected reactors: a dense fluidized bed endothermic gasifier (operating around 850 °C) which produces the syngas from biomass gasification, and an entrained bed exothermic reactor that burns a part of the residual char to provide heat to the gasifier. A bed material (sand, olivine or catalyst particles) circulates between the two reactors to transfer the heat.

During biomass gasification, the high temperature in the gasifier leads to the presence of refractory tars (tertiary tars) which contaminates the finally produced synthesis gas [3]. Indeed, they may lead to condensation, polymerization and clogging in the exit pipes. For instance, Table 1 gives the maximum tars concentration acceptable for different syngas applications. Besides, the works of de Sousa [4]

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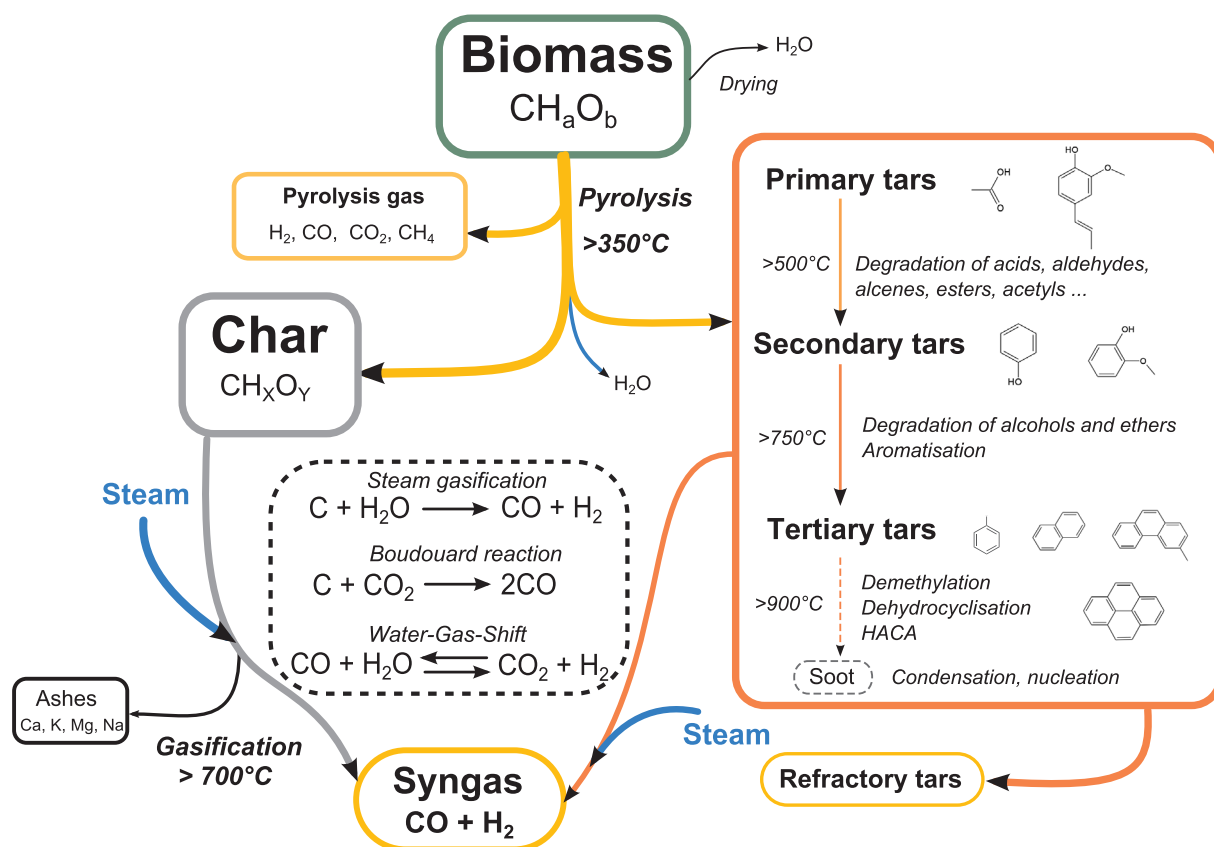


Fig. 1. Diagram of steam gasification of biomass and tars formation.

Table 1
Maximum tars concentration in the syngas for different applications.

Application	Maximum concentration	Ref.
IC Engines	100 mg.Nm ⁻³	[36]
Methanation process	5 mg.Nm ⁻³	[2,37]
Fischer-Tropsch	0.1 mg.Nm ⁻³	[38]

showed that, for gasification experiments in a fluidized bed reactor, the main tertiary tars are benzene, toluene and naphthalene.

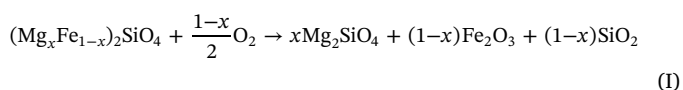
The removal of tars is a primordial technological barrier hindering the development of biomass gasification. Several approaches for tars removal can be found in the literature and are classified into two types: treatment inside the gasifier itself (primary methods) or gas cleaning outside the gasifier (secondary methods) [5]. The secondary methods include tars removal through chemical treatments either thermally or catalytically, or physical treatments such as tars condensation, gas/liquid separations or filtration [2]. Tars removal by secondary methods have been widely investigated and are well established in the literature [2,5]. The 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.

The use of catalytic solids in the gasifier has shown to be one of the best approaches to reduce tars content in the syngas [6]. Various catalysts were investigated in biomass gasification for tars conversion and have been discussed in several reviews [5,7–9]. Among them, calcined dolomite and olivine as well as Ni-based catalysts were found to have a strong catalytic activity.

A general agreement is drawn in the literature on the significant effect of dolomite as tars removal catalyst [10–13]. This natural solid is relatively inexpensive and disposable. Its calcination at high temperatures leads to the decomposition of the carbonate mineral to form MgO-CaO which is the main active catalytic component. However, this solid is not

appropriate for use in fluidized bed reactors due to its low attrition resistance.

Olivine is another natural inexpensive and disposable mineral with a global formula $(Mg_xFe_{1-x})_2SiO_4$. Many studies were carried out to determine and understand the catalytic effect of olivine [10,14–23]. For instance, some authors [12,18–23] compared results obtained from biomass gasification in a fluidized bed reactor with either olivine or inert sand particles. They concluded that the presence of olivine in the reactor leads to a lower tars content, a higher syngas yield, an increase in the H_2 and CO_2 content and a decrease in the amount of CO and CH_4 . They attributed this effect to the catalytic activity of olivine towards the tars removal and the Water-Gas-Shift reaction (Reaction (III)). In the literature [15,24], the catalytic performance of olivine is related to the presence of segregated iron at the particle surface which may have different oxidation states (i.e. iron(III), iron(II) and native iron). Devi et al. [15] mentioned that the calcination of olivine prior to experiments is essential and the presence of segregated iron is optimal for calcination at 900 °C and 10 h. For olivine calcination between 400 and 1100 °C, a part of the iron is ejected from the olivine structure according to the following reaction [24,25]:



Under reducing atmosphere, the reduction of Fe_2O_3 occurs in two steps [24,25]:

- the reduction of Fe_2O_3 into Fe_3O_4 for temperatures between 350 and 500 °C,
- the reduction of Fe_3O_4 into FeO and α -Fe between 500 and 900 °C.

Several researchers [11,17,26] concluded that iron is more active towards tars removal when its oxidation state is low. For instance,

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