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

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A B S T R A C T

The aim of the present work is to understand the different interactions which may occur between the char and a 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^{-3}), 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 ($\boldsymbol{R_p}$) is always smaller than the one of coke and char gasification ($\boldsymbol{R_{sr}} + \boldsymbol{R_g}$). 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 $\boldsymbol{P_{H_2}}/\boldsymbol{P_{H_2O}}$ 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

Nomenclature

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

steps (Fig. 1):

(1) A reduction step: In reducing atmosphere (H_2 or CO), the iron on the olivine surface is reduced to form reduced iron active sites (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, 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]:

$$C_mH_n(\text{aromatic}) = C_mH_x(\text{coke/soot}) + \frac{n-x}{2}H_2 \quad \text{(I)}$$

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 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 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:

$$C_mH_x(\text{coke}) + mH_2O \rightarrow mCO + \frac{x+2m}{2}H_2 \quad \text{(II)}$$

$$C(\text{char}) + H_2O \rightarrow CO + H_2 \quad \text{(III)}$$

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:

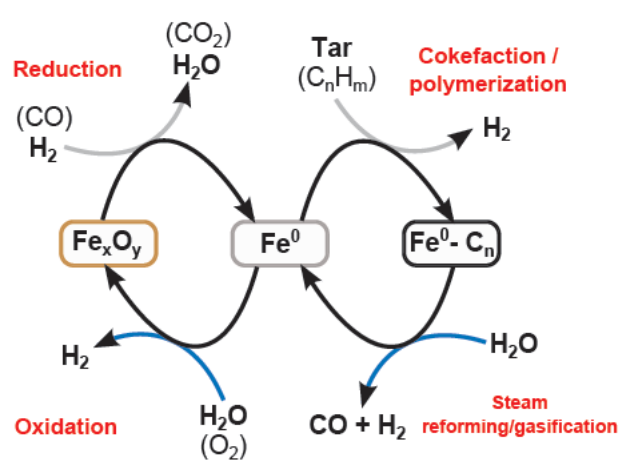

Fig. 1. Schematic diagram of the catalytic mechanism of olivine towards tars conversion [18].

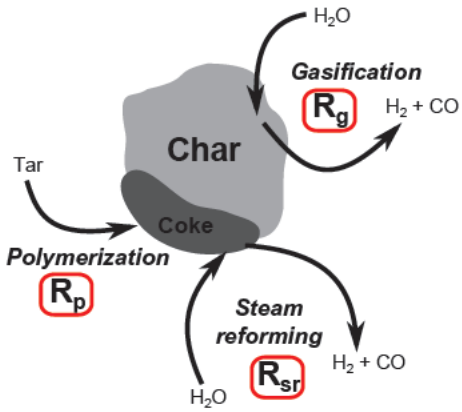

Fig. 2. Schematic diagram of the different interactions between char, tars and steam.

(1) The rate of tars polymerization (R_p) is higher than the one of coke and char consumption ($R_{sr} + R_g$). In this case, the char is progressively deactivated by coke accumulation onto its surface which blocks the pores and reduces the surface area of the catalyst [26]. For instance, during the decomposition of benzene and naphthalene at 900 °C in the absence of steam, Hosokai et al. [24] observed a strong formation of H_2 in the product gas which was explained by polymerization reactions. The coke was deposited onto the char surface. The average conversion of benzene and naphthalene was found to be 0.96 at the beginning of the experiment before gradually decreasing with time to reach 0.6 at 50 min. As no steam were present in the reactor ($R_{sr} = R_g = 0$), the authors concluded that the activity of char diminished due to coke formation.

(2) The rates of coke and char gasification with steam ($R_{sr} + R_g$) is higher than the one of tars polymerization (R_p). This phenomenon was highlighted by Fuentes Cano et al. [23] who reported that, during toluene and naphthalene conversion over a char bed at 950 °C and a steam partial pressure above 0.15 bars, the initial activity of char is maintained over the entire test. Hosokai et al. [25] also mentioned that the char activity is maintained if $R_{sr} + R_g$ is equivalent or greater than R_p. However, this is not necessary conditions for complete tars conversion.

Therefore, the char activity towards tars conversion depends on the temperature and the steam partial pressure in the reactor. These two parameters influence the kinetic of coke and char gasification. Hence, when the temperature and the steam partial pressure are increased, the kinetics of coke (R_{sr}) and char (R_g) gasification are favored.

Finally, Abu El Rub et al. [27] studied the effect of the type of catalysts in the reactor towards tars reduction. They compared biomass char with other catalysts (calcined dolomite, olivine, FCC catalyst, commercial nickel catalyst, silica sand and biomass ash) for the conversion of phenol and naphthalene. They concluded that the ranking of the different catalysts activity for naphthalene conversion at 900 °C is nickel > commercial biomass char > biomass char > biomass ash > FCC > dolomite > olivine > silica sand.

The aim of the present study is to understand the different interactions which may occur between the char and toluene in a fluidized bed reactor during the biomass gasification with steam in order to limit the amount of tars in the product gas. Experiments are conducted in a fluidized bed reactor 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 is investigated in the range of 0.05 to 0.4 bars and 0.0025 and 0.0075 bars (10.1 and 30.4 g.Nm^{-3}), respectively. A comparison between different media with or without char in the reactor on toluene conversion is also proposed.

Table 1
Physicochemical properties of the solids.

	Sand	Olivine	Char
Composition (db,wt%)	SiO_2: 98.34% Fe_2O_3: 0.022% Al_2O_3: 1.206% TiO_2: 0.03% CaO: 0.014% K_2O: 0.745%	MgO: 57.5–50.0% SiO_2: 39.0–42.0% CaO: max 0.4% Fe_2O_3: 8.0–10.5%	C: 86.65% H: 2.14% O: 6.09% Ash: 5.12%
Chemical formula	SiO_2	$(Mg_{1-x}Fe_x)_2SiO_4$	$CH_{0.30}O_{0.05}$
d_{32} (µm)	246	264	–
Apparent density ρ_p (kg.m^{-3})	2400 ± 20	2965 ± 20	600 ± 20
True density ρ_t (kg.m^{-3})	2650 ± 2	3265 ± 2	1604 ± 8
Solid porosity ε_p (%)	9	9	63
U_{mf} (850 °C) (cm.s^{-1})	2.9	3.7	–

2. Experimental section

2.1. Solid media

The physicochemical properties of the different solids used in this study are presented in Table 1. The apparent density was measured by mercury porosimetry while the true density was determined by helium pycnometry.

The olivine was purchased from the Austrian Company Magnolithe Gmbh. After receipt, the particles were calcined at 900 °C for 4 h in a fluidized bed reactor before being sieved between 200 and 300 µm. The minimum fluidization velocity (U_{mf}) of olivine was measured experimentally with nitrogen and is equal to 3.7 cm/s at 850 °C.

The sand was purchased from SIBELCO Company and was calcined following the same procedure. After calcination, the particles were sieved to obtain a size between 200 and 300 µm.

The char was obtained from pyrolysis of pine wood under nitrogen at 650 °C in a screw reactor for 1 h. The heating rate of the wood particles was fixed and is equal to 50 °C/min. The shape of the produced char is cylindrical (D = 4 mm, L = 9 mm).

2.2. Experimental setup

The experimental setup is shown in Fig. 3 and has been presented in detail in a previous paper [18]. Briefly, the fluidized bed reactor consists of a refractory steel tube of 5.26 cm of internal diameter and 94 cm of height, heated by an electric furnace delivering 2.6 kW of electric power. About 580 g of particles (sand or olivine) are used as fluidized solids. The corresponding static bed height is equal to 17 cm.

The fluidizing gas flow rates of N_2 and H_2 are measured by two mass flow meters. Liquid water and toluene are fed by two pumps Gilson 305. The water is mixed to the gases (i.e. N_2 and H_2) before being vaporized in a tube forming a coil around the reactor. Then, preheated gases enter a wind box beneath the reactor in which the toluene is continuously injected and vaporized. For experiments at 850 °C and a gas velocity equal to 7 times the minimum fluidization velocity of olivine, the wind box temperature is between 300 °C and 400 °C. Preliminary experiments showed that both water and toluene were totally vaporized before entering the reactor. The gas distribution in the bed is done by a perforated plate of 19 orifices equipped at its base with a stainless steel sieve of 30 µm of mesh. At the reactor outlet, the elutriated particles and condensable gases are collected by a cyclone and a condenser, respectively.

The temperature inside the fluidized bed is controlled by two thermocouples located at 5 and 25 cm above the distributor. The former is used to regulate the temperature of the reactor using a PID controller. A differential pressure transmitter is connected at 5 and 500 mm above the distributor in order to follow the pressure drop of the bed.

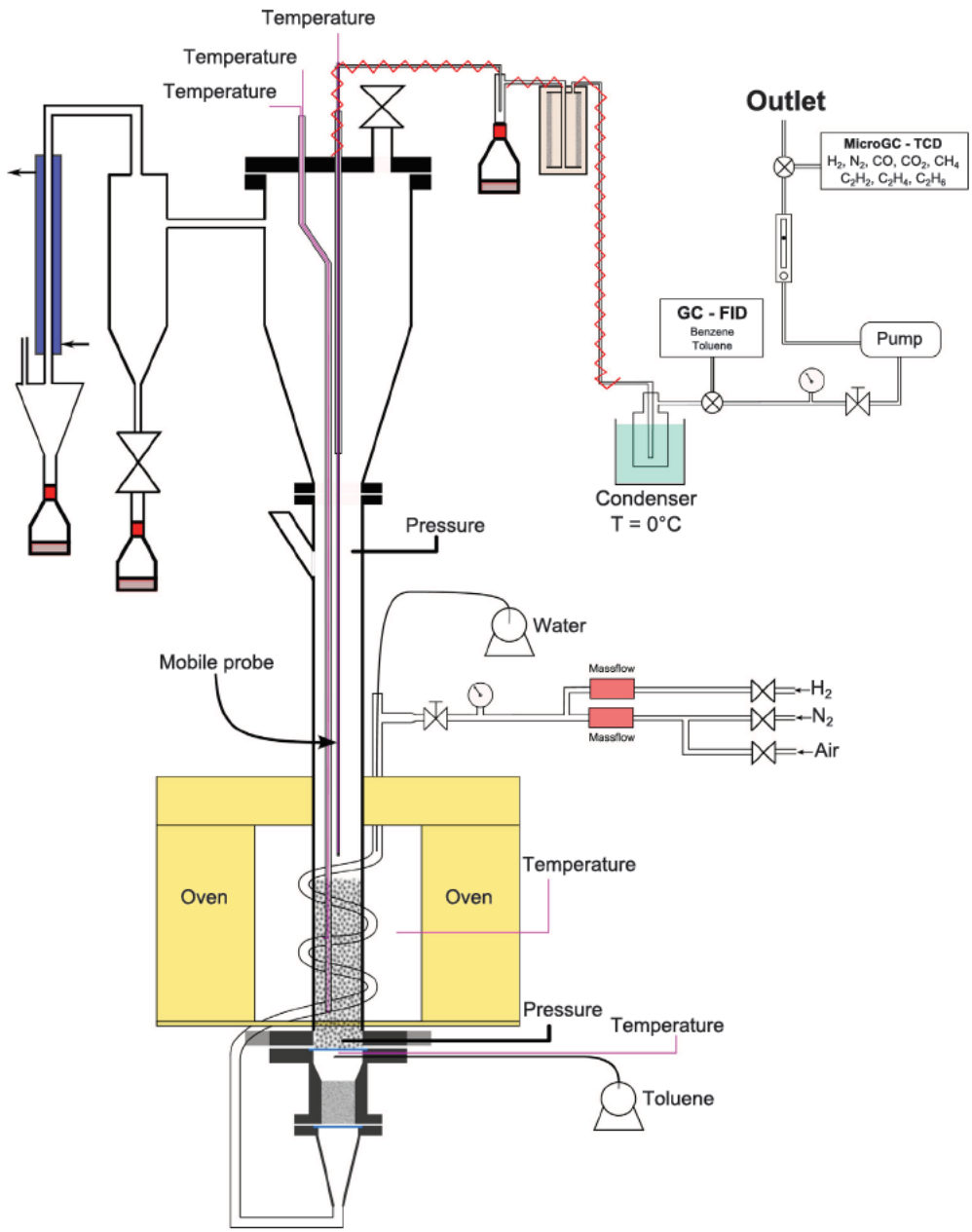

Fig. 3. Experimental setup used for toluene conversion.

2.3. Sampling method and gas analysis

The sampling of gases is carried out by a stainless steel mobile probe located at the fluidized bed surface. A thermocouple is placed inside the mobile probe to measure the precise temperature at the entrance of the probe. The gas sample is sucked by a vacuum pump connected to a flowmeter (constant volume flow of 100 mL.min^{-1} at STP). At the mobile probe outlet, the pumped gas is filtered and condensed at 0 °C. At this temperature, theoretical condensation of toluene occurs when its partial pressure exceeds 0.0093 bars. To prevent any condensation of steam, all of the lines from the reactor to the entrance of the con densation system are heated to a temperature of 150 °C.

The sample is sent online to a Gas Chromatograph (GC) Thermoscience GC Ultra Trace equipped with a 30 m × 0.53 mm ID 0.5 µm capillary TR 5 column with 5% Phenyl Methylpolysiloxane he ated at 60 °C for 6 min. A Flame Ionization Detector (FID) enables the quantification of both benzene and toluene.

A micro Gas Chromatograph (micro GC) is used to online analyze the non condensable gases. It is equipped with a Poraplot U 10 m × 0.25 mm ID column connected to a Thermal Conductivity Detector (TCD) calibrated for CO_2 quantification. A CP Molsieve 5A 10 m × 0.25 mm column connected to a TCD is calibrated for the analyses and the quantification of N_2, H_2, O_2, CH_4 and CO. The time lapse between two quantifications is about 3 min.

2.4. Operating conditions and data treatment

Tests were conducted at atmospheric pressure and a temperature of 850 °C. The total molar flow rate at the entrance of the reactor was kept constant and equal to 0.35 mol.min^{-1} so that the gas velocity was set to 7 times the minimum fluidization velocity of olivine at 850 °C. From this value, the gas residence time considering an empty reactor is 0.7 s. Based on literature data regarding the amount of tar during biomass gasification [1,34], the toluene partial pressure in the reactor was varied between 0.0025 and 0.0075 bars which corresponds to 10.1 and 30.4 g.Nm^{-3}.

For experiments with char, it was first loaded in the reactor. The amount of char was fixed to 17.4 g which represents 3% of the solid medium weight and 15% of the bed volume. This value is commonly used in the gasifier in FICFB processes. The reactor was heated under a pure flow of nitrogen to a temperature of 850 °C. Once a steady state was achieved, the gas was switched from nitrogen to a mixture of N_2/H_2O to start the steam gasification of char. For tests with toluene, after a few minutes of char gasification with steam, the reactive gas atmosphere was switched from N_2/H_2O to a mixture of $N_2/H_2O/C_7H_8$ with the same total molar flow rate. Each test was performed during 1 h to enable better comparison of the results. Besides, this time is much higher than the char residence time in the gasifier during biomass gasification in FICFB process which is in the range of 5 to 10 min.

The different operating conditions of each experiment are presented in Table 2. Seven sets of experiments were performed:

- Experiments GS 1 study the effect of steam partial pressure on the char gasification at 850 °C in the presence of sand particles. This set of tests is taken as a reference.
- Experiments GS 2 investigate the influence of steam partial pressure on the char gasification in the presence of sand particles with a constant toluene partial pressure at the entrance of the reactor fixed to 0.005 bars.
- Experiments GS 3 carried out the study on the effect of toluene partial pressure between 0.0025 and 0.0075 bars during the char gasification with a constant steam partial pressure of 0.2 bars and sand as fluidized solid.
- Experiments GO 4 is similar to the Experiments GS 2. However, olivine particles are used as fluidized medium in the fluidized bed reactor.
- Sets S 1 and O 1 study the effect of steam on toluene conversion with sand or olivine as fluidized medium and without char in the reactor. The toluene partial pressure is fixed to 0.005 bars.
- Finally, a set of experiments O 2 was carried out to investigate the effect of the steam partial pressure with a constant hydrogen partial pressure of 0.2 bars on toluene conversion in the presence of olivine particles.

For each experiment, the composition of both the non condensable gases and the tars are analyzed as a function of time. The nitrogen is not involved during the char gasification and is only used as an inert gas for mass balances. From the measured molar percentages of nitrogen at the reactor outlet, the total molar flow rate is calculated according to the following expression:

$$\dot{n}_t(t) = \frac{\dot{n}_{N_2}}{x_{N_2}(t)} \tag{1}$$

where $\dot{n}_t(t)$ is the total molar flow rate (mol.min^{-1}), $\dot{n}_{N_2}$ represents the molar flow rate of nitrogen at the entrance of the reactor (mol.min^{-1}) and $x_{N_2}(t)$ is the measured molar fraction of nitrogen at the reactor outlet.

The partial molar flow rate of each component is calculated as follows:

$$\dot{n}_i(t) = x_i(t)\cdot\dot{n}_t(t) \tag{2}$$

where $\dot{n}_i(t)$ and $x_i(t)$ are the instantaneous partial molar flow rate and molar fraction of component i at the reactor outlet, respectively (i = H_2, CO, CO_2, CH_4, C_6H_6, C_7H_8).

- In the case of char gasification in the presence of steam (set GS 1), the detected components in the product gas were found to be H_2, CO, CO_2 and a small amount of CH_4. The carbon containing gases molar flow rate at the reactor outlet ($\dot{n}_{c,gasi}(t)$) is determined by the following equations:

$$\dot{n}_{c,gasi}(t) = \dot{n}_{CO}(t) + \dot{n}_{CO_2}(t) + \dot{n}_{CH_4}(t) \tag{3}$$

The normalized carbon containing gases molar flow rate and the normalized cumulative amount of carbon containing gases at time t are respectively given by:

$$\frac{\dot{n}_{c,gasi}(t)}{n^{in}_{c,char}} = \frac{dX_c}{dt} = R_g \tag{4}$$

$$\overline{n}_{c,gasi} = X_c = \frac{\int_{t=0}^{t} \dot{n}_{c,gasi}(t)dt}{n^{in}_{c,char}} \tag{5}$$

where $n^{in}_{c,char}$ is the amount of carbon in the introduced char (mol), X_c and dX_c/dt are the carbon conversion rate and the instantaneous gasification rate, respectively.

- In the case of char gasification in the presence of steam and toluene (sets GS 2, GS 3 and GO 4), the detected components in the product gas are H_2, CO, CO_2, CH_4, C_6H_6 and unconverted toluene. The formation of benzene is attributed to the hydrodealkylation and the steam dealkylation reactions according to the following reactions:

$$C_7H_8 + H_2 \rightarrow C_6H_6 + CH_4 \tag{IV}$$

$$C_7H_8 + H_2O \rightarrow C_6H_6 + CO + 2H_2 \tag{V}$$

The toluene may also react on the char surface according to Reaction (I) to produce a carbonaceous deposit which is further converted by steam reforming of coke according to Reaction (II). The formation of CH_4 is very low during each experiment and may originate from both the hydrodealkylation reaction (Reaction (IV)) and the interactions between char and hydrogen [35].

The toluene conversion rate, noted $X_{toluene}$, is defined as the ratio between the molar flow rate of converted toluene and the one of introduced C_7H_8:

$$X_{toluene} = \frac{\dot{n}^{in}_{C_7H_8} - \dot{n}_{C_7H_8}}{\dot{n}^{in}_{C_7H_8}} \tag{6}$$

Table 2
Operating conditions of each experiment, 850 °C and F_{tot} = 0.35 mol.min^{-1}.

Exp. –	P_{H2} (bar)	P_{H2O} (bar)	P_{N2} (bar)	P_{C7H8} (bar)	Medium –	Char (g)
GS 1a	0	0.05	0.95	0	Sand	17.4
GS 1b	0	0.1	0.90	0	Sand	17.4
GS 1c	0	0.2	0.80	0	Sand	17.4
GS 1d	0	0.4	0.60	0	Sand	17.4
GS 2a	0	0.05	0.945	0.005	Sand	17.4
GS 2b	0	0.1	0.895	0.005	Sand	17.4
GS 2c	0	0.2	0.795	0.005	Sand	17.4
GS 2d	0	0.4	0.595	0.005	Sand	17.4
GS 3a	0	0.2	0.595	0.0025	Sand	17.4
GS 3b	0	0.2	0.795	0.005	Sand	17.4
GS 3c	0	0.2	0.895	0.0075	Sand	17.4
GO 4a	0	0.05	0.945	0.005	Olivine	17.4
GO 4b	0	0.1	0.895	0.005	Olivine	17.4
GO 4c	0	0.2	0.795	0.005	Olivine	17.4
GO 4d	0	0.4	0.595	0.005	Olivine	17.4
S 1a	0	0.4	0.595	0.005	Sand	–
S 1b	0	0.2	0.795	0.005	Sand	–
S 1c	0	0.1	0.895	0.005	Sand	–
S 1d	0	0.05	0.945	0.005	Sand	–
O 1a	0	0.4	0.595	0.005	Olivine	–
O 1b	0	0.2	0.795	0.005	Olivine	–
O 1c	0	0.1	0.895	0.005	Olivine	–
O 1d	0	0.05	0.945	0.005	Olivine	–
O 2a	0.2	0.4	0.395	0.005	Olivine	–
O 2b	0.2	0.2	0.595	0.005	Olivine	–
O 2c	0.2	0.1	0.695	0.005	Olivine	–
O 2d	0.2	0.05	0.745	0.005	Olivine	–

where $\dot{n}_{C_7H_8}$ and $\dot{n}^{in}_{C_7H_8}$ are the partial molar flow rates of toluene at the reactor outlet and inlet, respectively (mol.min^{-1}). For each experiment, these partial molar flow rates were calculated once they have reached a constant value.

The selectivity of benzene is calculated according to the equation below:

$$S_{C_6H_6} = \frac{6 \cdot \dot{n}_{C_6H_6}}{7 \cdot (\dot{n}^{in}_{C_7H_8} - \dot{n}_{C_7H_8})} \tag{7}$$

where $\dot{n}_{C_6H_6}$ is the molar flow rate of benzene (mol.min^{-1}).

In this work, it was found that the CO and the CH_4 selectivities from toluene conversion are very low. Therefore, it was assumed that $(1-S_{C_6H_6})$ represents the selectivity of the produced coke from toluene polymerization (Reaction (I)). The rate of tars polymerization (R_p) is obtained according to:

$$R_p = \frac{7 \cdot X_{\text{toluene}} \cdot \dot{n}^{in}_{C_7H_8} - S_{C_6H_6} \cdot 7 \cdot (\dot{n}^{in}_{C_7H_8} - \dot{n}_{C_7H_8})}{n^{in}_{c,char}} \tag{8}$$

where R_p is the rate of tars polymerization (mol.min^{-1}.mol^{-1}).

The carbon containing gases molar flow rate at the reactor outlet ($\dot{n}_{c,gas+tol}(t)$) is determined by the following equations:

$$\dot{n}_{c,gas+tol}(t) = \dot{n}_{CO}(t) + \dot{n}_{CO_2}(t) + \dot{n}_{CH_4}(t) \tag{9}$$

Again, the normalized carbon containing gases molar flow rate and the normalized cumulative amount of carbon containing gases at time t are respectively given by:

$$\frac{\dot{n}_{c,gas+tol}(t)}{n^{in}_{c,char}} = R_{sr} + R_g \tag{10}$$

$$\overline{n}_{c,gas+tol} = \frac{\int_{t=0}^{t} \dot{n}_{c,gas+tol}(t)\,dt}{n^{in}_{c,char}} \tag{11}$$

3. Results and discussion

3.1. Steam gasification of char without toluene (experiments GS 1)

The results of the steam gasification of char in a fluidized bed reactor at 850 °C with a steam partial pressure of 0.4 bars (experiment GS 1d) are given in Fig. 4 (A) which presents the molar flow rates of H_2, CO, CO_2 and CH_4 versus time. First, this figure highlights that the molar flow rates of H_2 and CH_4 decrease with time while the ones of CO and CO_2 decrease for the first 25 min before reaching a constant value. Besides, H_2 is the larger produced component during the steam gasification of char. A large amount of CO and CO_2 is also produced. These three compounds are the results of the steam gasification of carbon (Reaction (III)) and the Water Gas Shift reaction (Reaction (V)):

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{V}$$

A small amount of CH_4 was also detected. As mentioned previously, it can be explained by interactions between carbon and hydrogen in the reactor [35]. Similar results were obtained for experiments with a steam partial pressure in the range of 0.05 0.2 bars. Besides, it was found that the molar flow rates of each component increase by raising the steam partial pressure.

The effect of steam partial pressure on the carbon conversion rate is presented in Fig. 4 (B). It can be seen that a raise of this parameter increases X_c. Besides, after approximately 20 min, the carbon conversion rate shows a linear profile versus time which indicates a constant instantaneous gasification rate during the reaction.

3.2. Interactions between char and toluene

3.2.1. Effect of steam partial pressure with $P_{C_7H_8} = 0.005$ bars (experiments GS 2)

As discussed in the introduction, interactions between char and tars can be summarized according to Fig. 2. Hence, during an experiment in the presence of char and toluene in the reactor, two competing phenomena take place: the presence of char favors the toluene conversion while the presence of toluene hinders the char gasification with steam.

Fig. 5 (A) presents the molar flow rates of H_2, CO, CO_2 and CH_4 versus time during the gasification of char with a steam partial pressure of 0.4 bars and in the presence of 0.005 bars of toluene (experiment GS 2d). The black line in the figure indicates the beginning and the end of the toluene injection. During this injection, the total molar flow rate at the entrance of the reactor does not change. The molar flow rates of both toluene and nitrogen are adjusted in order to obtain a toluene partial pressure of 0.005 bars in the gas stream. From Fig. 5 (A), it can be seen that the addition of toluene in the reactor increases the molar flow rates of CH_4 and H_2 during the first 15 min after the toluene injection before gradually decreasing. This result can be attributed to the reaction of toluene polymerization according to Reaction (I) which produces large amounts of hydrogen. The raise of the methane molar flow rate is attributed to the hydrodealkylation reaction between toluene and H_2 (Reaction (IV)). Besides, it was found that the presence of toluene has no effect on the molar flow rates of CO and CO_2 which indicates that the rate of char gasification is not influenced by this parameter.

Fig. 5 (B) shows the molar flow rates of both benzene and toluene during the experiment GS 2d. This figure highlights that the toluene molar flow rate increases during the first 15 min after the toluene injection before reaching a constant value. This result emphasizes that the char strongly favors the toluene polymerization at the beginning of the

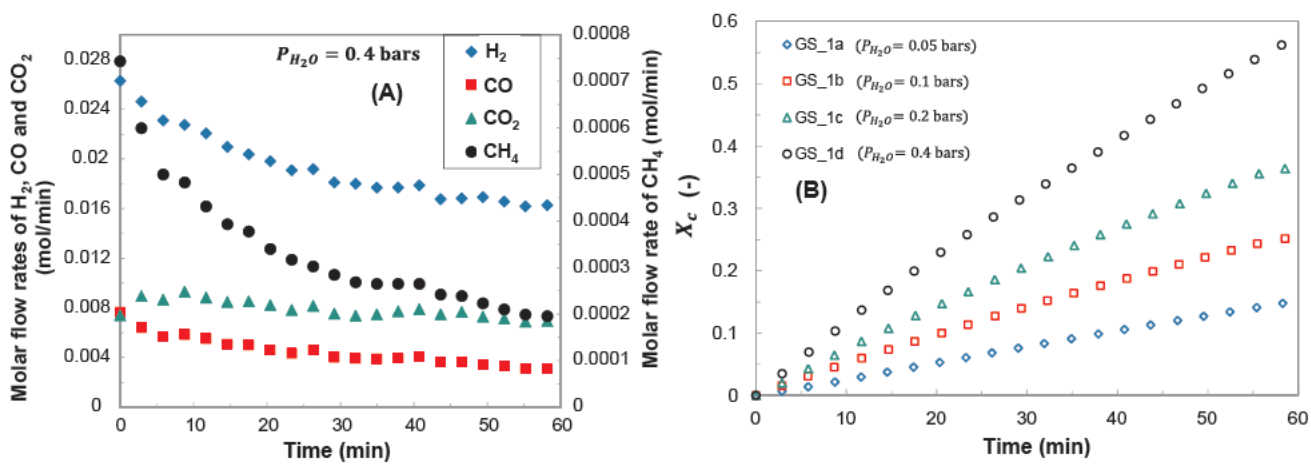

Fig. 4. (A) Molar flow rates of H_2, CO, CO_2 and CH_4 versus time during the experiment GS 1d, (B) carbon conversion rate versus time during the experiments GS 1.

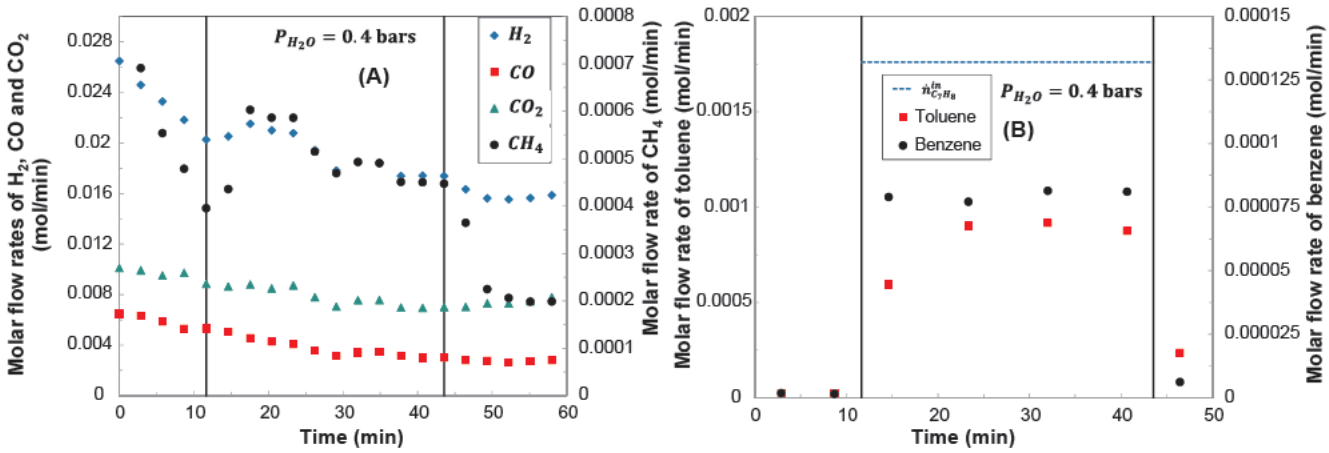

Fig. 5. (A) Molar flow rates of H_2, CO, CO_2 and CH_4 versus time during the steam gasification of char in the presence of toluene, (B) molar flow rates of benzene and toluene versus time, the black line indicates the beginning and the end of the toluene injection (experiment GS 2d).

reaction before partially losing its catalytic activity. After 15 min of toluene injection, the char activity is stabilized and the toluene molar flow rate has reached a constant value. In this case, the reaction of tar polymerization leads to a decrease in the amount of active sites on the char surface while the presence of steam tends to continuously maintain the catalytic activity of the solid by coke and char gasification. Therefore, a competing effect between deactivation and regeneration of active sites on the char surface occurs in the reactor. Besides, the molar flow rate of benzene is constant during the experiment which highlights that Reaction (IV) takes place.

Fig. 6 presents the effect of steam partial pressure on the toluene conversion (X_{toluene}), the selectivity of benzene ($S_{C_6H_6}$) and the rate of tars polymerization (R_p). It can be seen that, an increase in the steam partial pressure gives rise to:

- an increase in the toluene conversion. For instance, X_{toluene} is equal to 0.18, 0.21, 0.38 and 0.49 for a steam partial pressure of 0.05, 0.1, 0.2 and 0.4 bars, respectively. This effect may be explained by the influence of steam partial pressure on both the reactions of steam reforming of coke and gasification of char as well as the steam dealkylation of toluene. Indeed, an increase in P_{H_2O} favors Reactions (II) and (III) and maintains the catalytic activity of char by continuously generating active sites on its surface. Therefore, more toluene is converted on the reactive solid.
- a decrease in the selectivity of benzene and an increase in the selectivity of coke. As the catalytic activity of char is maintained with the steam partial pressure, more toluene can be polymerized on the char surface which leads to a higher production of coke. As a consequence, the selectivity of benzene decreases while the one of coke increases.
- a raise of the rate of tars polymerization. This result is also due to the effect of steam partial pressure on the rates of char and coke gasification ($R_{sr} + R_g$). Indeed, a higher P_{H_2O} favors these reactions and promotes the formation of active sites which fosters the tars polymerization [24,26].

3.2.1.1. Comparison between R_{sr} and R_g. Fig. 7 presents the effect of steam partial pressure on the two normalized cumulative amount of carbon containing gases ($\overline{n}_{c,gasi}$ and $\overline{n}_{c,gasi+tol}$, see Eqs. (5) and (10)) versus time. The open and filled symbols correspond to experiments without and with toluene, respectively while the vertical lines represent the toluene injection time. It can be seen that the addition of toluene in the gas stream has no influence on the total amount of CO, CO_2 and CH_4. The two curves almost coincide. Besides, $\overline{n}_{c,gasi}$ and $\overline{n}_{c,gasi+tol}$ show a linear profile versus time.

The difference between the rate of steam reforming of coke R_{sr} and the one of char gasification R_g is highlighted in Fig. 8. This figure plots the normalized carbon containing gases molar flow rate (i.e. $R_{sr} + R_g$, see Eq. (10)) versus the instantaneous gasification rate (Eq. (5)) for each steam partial pressure. These parameters were calculated from the slope of the straight line in Fig. 4 (B) and Fig. 7. First, it was found that $R_{sr} + R_g$ and R_g increase by raising the steam partial pressure as the steam gasification of both coke and char is favored with P_{H_2O}. Results given in Fig. 8 show a linear profile between the two consumption rates. Hence, the following relation can be written:

$$R_{sr} + R_g = \alpha \cdot R_g \tag{12}$$

where α is obtained from the slope of the straight line. It is equal to 1.03. This result emphasizes that the normalized carbon containing gases molar flow rate ($R_{sr} + R_g$) is slightly higher than the one of instantaneous gasification rate R_g. Therefore, it can be concluded that the rate of steam reforming of coke R_{sr} is much lower than the one of char gasification R_g (Eq. (12)). As a consequence, the carbonaceous solid deposit produced by tars polymerization is much less reactive than the initial char.

$$R_{sr} = 0.03 \cdot R_g \tag{13}$$

3.2.1.2. Comparison between R_c and R_g. From Fig. 2, the rate of coke deposition R_c is defined by the following expression. It corresponds to the normalized molar flow rate of unconverted coke during each experiment

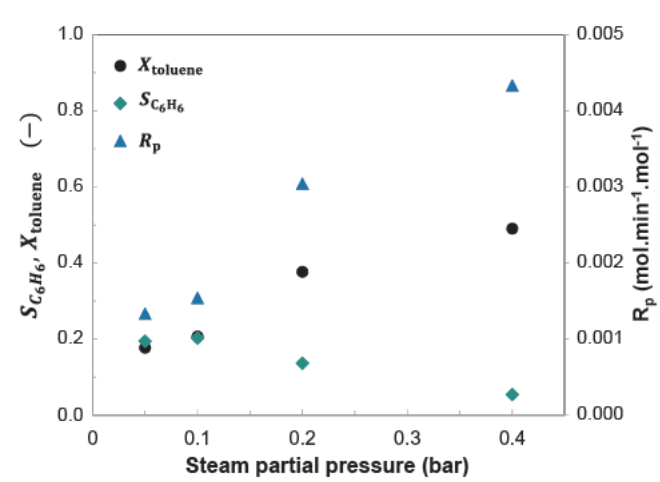

Fig. 6. Effect of steam partial pressure on $X_{toluene}$, $S_{C_6H_6}$ and R_p (experiment GS 2).

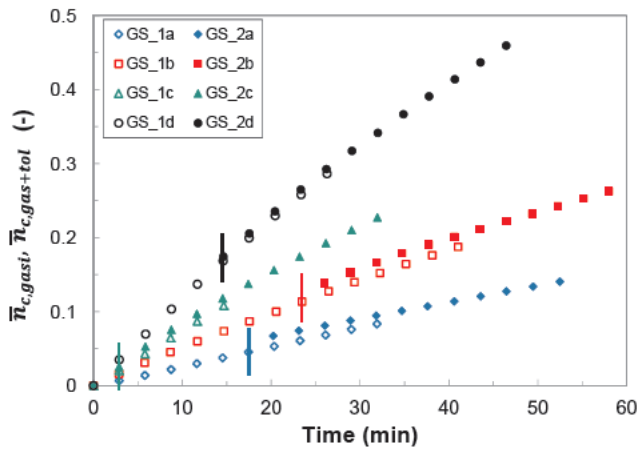

Fig. 7. Comparison between the cumulative amount of carbon versus time with and without toluene in the gas stream (experiments GS 1 and GS 2), the black line indicates the beginning of the toluene injection.

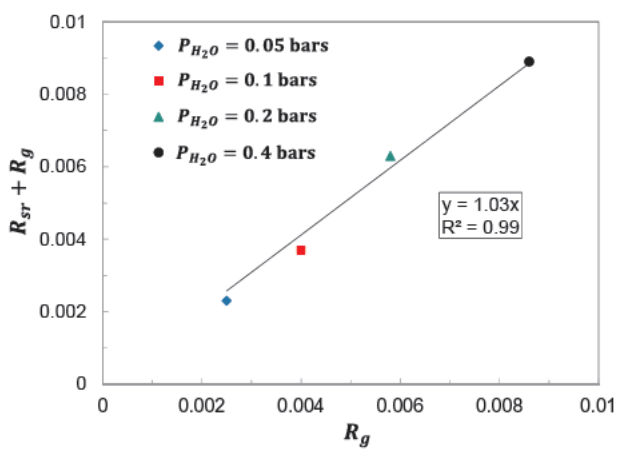

Fig. 8. Effect of steam partial pressure on the normalized carbon-containing gases molar flow rate ($R_{sr} + R_g$) versus char gasification rate (R_g), determination of α.

$$R_c = R_p - R_{sr} \tag{14}$$

By combining Eqs. (8) and (10), $R_g - R_c$ can be calculated as follows:

$$R_g - R_c = \frac{\dot{n}_{c,gas+tol}(t) - 7\cdot(\dot{n}^{in}_{C_7H_8} - \dot{n}_{C_7H_8}) - 6\cdot\dot{n}_{C_6H_6}}{n^{in}_{c,char}} \tag{15}$$

Fig. 9 plots $R_g - R_c$ versus R_g for different steam partial pressures. Several observations can be made:

- $R_g - R_c$ is positive which indicates that $R_g > R_c$ for each steam partial pressure. Therefore, the amount of carbonaceous solid (char + coke) in the reactor always decreases during the experiment and the char activity is maintained. However, as mentioned by several authors [24], this condition does not necessary lead to complete toluene conversion (see Fig. 6).
- $R_g - R_c$ increases by raising the steam partial pressure. This indicates that P_{H_2O} has a greater influence on R_g compared to R_c.
- A linear profile between $R_g - R_c$ and R_g is obtained. Hence, the following relation can be written:

$$R_g - R_c = \beta\cdot R_g \tag{16}$$

where β is obtained from the slope of the straight line. It is equal to 0.45. Therefore, it can be concluded that the rate of coke deposition is lower (by more than half) than the rate of char gasification:

$$R_c = 0.55\cdot R_g \tag{17}$$

3.2.2. *Effect of toluene partial pressure*

A set of tests was conducted in order to investigate the effect of toluene partial pressure during experiments at 850 °C with a steam partial pressure of 0.2 bars (experiment GS 3).

Fig. 10 (A) shows the effect of toluene partial pressure on the toluene conversion ($X_{toluene}$), the selectivity of benzene ($S_{C_6H_6}$) and the rate of tars polymerization (R_p). It can be observed that the toluene conversion decreases as the toluene partial pressure is increased. This is the result of the char losing its catalytic activity due to coke deposition inside the pores [26]. As a consequence, the selectivity of coke slightly decreases while the one of benzene increases. Finally, as more toluene is introduced in the reactor, the rate of tars polymerization increases by raising the toluene partial pressure.

Fig. 10 (B) presents the effect of toluene partial pressure on $R_g - R_c$. It can be observed that this parameter is positive and continuously decreases by raising the toluene partial pressure. These results emphasize that, for a toluene partial pressure up to 0.0075 bars:

- the rate of char gasification is higher than the one of coke deposition $R_g > R_c$;
- the amount of solid carbon in the reactor continuously decreases during each experiment;
- the char has not completely lost its catalytic activity.

Besides, as the toluene partial pressure is increased, R_c progressively increases. It may be assumed that for a toluene partial pressure higher than 0.0075 bars, the rate of coke deposition (R_c) would become higher than the rate of char gasification (R_g). In this case, the amount of carbonaceous solid in the reactor would increase and a steam partial pressure of 0.2 bars would not be sufficient to refresh the char which would lose its catalytic activity.

3.3. *Comparison between char, sand and olivine*

This section aims to compare the effect of the solid media and the steam partial pressure on the amount of tar in the product gas for a given toluene partial pressure of 0.005 bars at the entrance of the fluidized bed reactor. The comparison has been based on the parameter R_T which represents the normalized rate of carbon containing tars (C_6H_6 and C_7H_8) at the reactor outlet. It is defined as follows:

$$R_T = \frac{6\cdot\dot{n}_{C_6H_6} + 7\cdot\dot{n}_{C_7H_8}}{7\cdot\dot{n}^{in}_{C_7H_8}} \tag{18}$$

Therefore, the purpose is to determine the proper operating conditions (i.e. solid materials and reactive gas atmosphere in the reactor) to employ during the steam gasification of biomass in order to limit the amount of tar in the product gas.

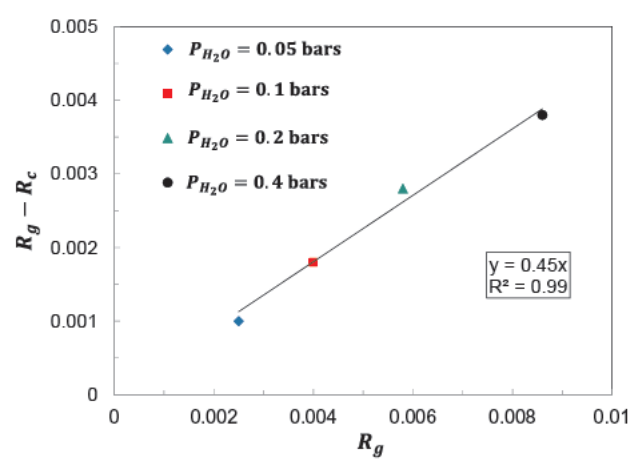

Fig. 9. $R_g - R_c$ versus R_g for different steam partial pressures, determination of β.

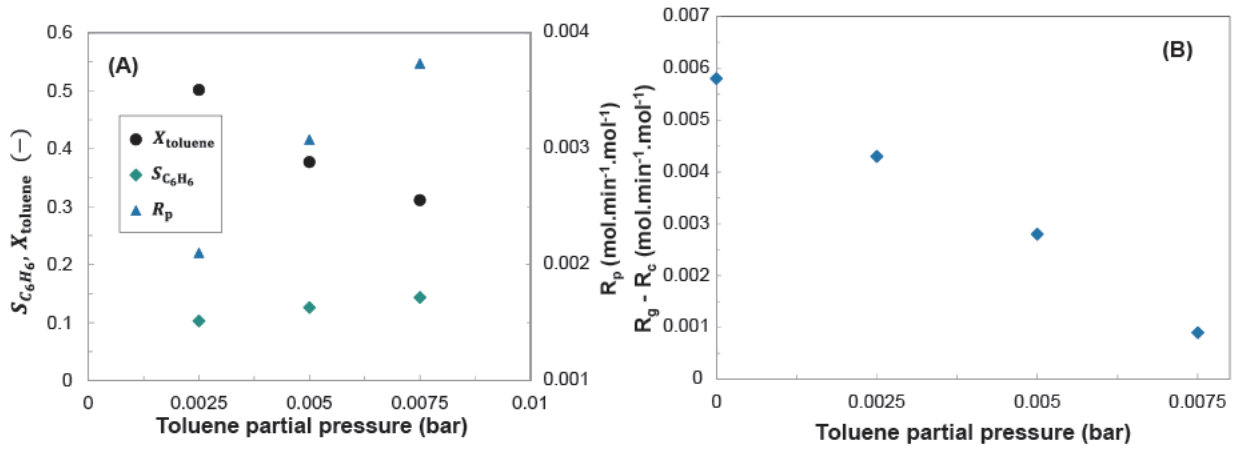

Fig. 10. Effect of toluene partial pressure on (A) $X_{toluene}$, $S_{C_6H_6}$ and R_p, (B) R_g–R_c (experiments GS 3).

The sets of experiments GS 2, GO 4, S 1, O 1 and O 2 were used for the comparison. For experiments with char in the fluidized bed reactor, the parameter R_T was determined once the molar flow rates of both benzene and toluene in the product gas have reached a constant value. In this case, the R_T calculated is considered as the one which will be obtained for steady state experiments.

Fig. 11 presents the effect of steam partial pressure on R_T for different solid media in the reactor. Several observations can be drawn:

- For experiments without char in the reactor, the steam partial pressure has no influence on toluene conversion over sand and olivine. A constant R_T of 99% and 85% is obtained in the case of tests with sand (♦) and olivine particles (▲), respectively.
- Experiments O 2 investigates the effect of steam partial pressure for a constant hydrogen partial pressure of 0.2 bars. Results show that a very small value of R_T (< 1%) is obtained when the steam partial pressure is 0.05 bars. When the steam partial pressure is raised, R_T increases before reaching a constant value for $P_{H_2O} > 0.2$ bars. This phenomenon can be explained by the catalytic mechanism of olivine towards toluene conversion which has been given in Fig. 1. Indeed, olivine particles show a strong catalytic activity when the ratio P_{H_2}/P_{H_2O} in the reactive atmosphere is above 1.5. In this case, very small amounts of benzene are produced and toluene conversion is very high (Fig. 11). For a ratio up to 1.5, R_T is almost constant and equal to about 80% (●).
- For experiments with a mixture of sand + 3% char (■) (experiment GS 2) and olivine + 3% char (✕) (experiment GO 4), it was found that the presence of this carbonaceous solid in the reactor improves the tars conversion. In particular, it was shown that the steam partial pressure is a key parameter for tars degradation which influences the competition between the rate of coke deposition (R_c) and the rate of char gasification with steam (R_g). When the steam partial pressure is increased, the toluene conversion increases while the benzene selectivity decreases which highlights a higher catalytic activity of the char.

It is important to note that the amount of char in each experiment was fixed to 17.4 g which represent 3% of the fluidized bed mass. It can be assumed that a higher amount of char may significantly improve the tars conversion. Besides, in this work, a char residence time of 60 min in the reactor is used which is much higher than the one of industrial gasifiers. Hence, in industrial conditions, it can be assumed that the catalytic activity of char is higher and more interactions between char and tars occur. Therefore, results given in Fig. 11 in the presence of char may be overestimated.

From results obtained in Fig. 11, it can be seen that the best method to limit the amount of tars is to increases the ratio P_{H_2}/P_{H_2O} in the reactor. In FICFB process, P_{H_2O} and P_{H_2} are less than 0.3 bars and 0.15 bars, respectively. Consequently, one way to control the ratio P_{H_2}/P_{H_2O} in the gasifier would be to reinject the produced syngas which would lead to an increase in the reducing gas atmosphere and a decrease in the steam partial pressure.

4. Conclusion

This paper presented an experimental study regarding the effect of steam and toluene partial pressures on the steam gasification of a biomass char in a fluidized bed reactor. The purpose was to understand the different interactions which occur between toluene and char in a reactive atmosphere representative of biomass gasification processes.

Experiments were performed at 850 °C and atmospheric pressure with sand particles as solid medium. The steam partial pressure was varied between 0.05 and 0.4 bars while the one of toluene was studied between 0.0025 and 0.0075 bars.

Results showed that the presence of toluene in the gas stream during the char gasification with steam leads to:

- an increase in the H_2 production which is the result of tars polymerization on the char surface leading to the formation of a carbonaceous solid (coke). This coke is much less reactive towards steam gasification than the initial char.
- a raise of the CH_4 and benzene production which is attributed to the hydrodealkylation of toluene.

For the operating conditions used in this work, the rate of coke

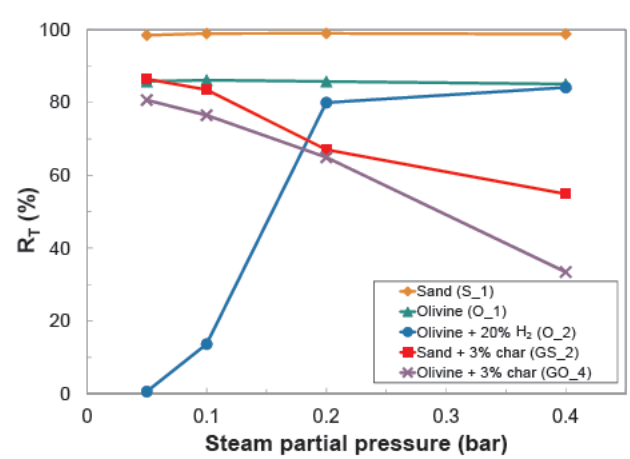

Fig. 11. Normalized rate of carbon-containing tars (R_T) versus steam partial pressure for different solid media in the reactor, 850 °C, P_{tol} = 0.005 bar.

deposition (R_c) was found to be lower than the one of char gasification (R_g) indicating that the catalytic activity of char is maintained. Besides, it was found that an increase in the steam partial pressure yields to a raise of the toluene conversion rate and a decrease in the selectivity of benzene.

Finally, a comparison between different solid catalysts in the flui dized bed reactor showed that two operating conditions may be em ployed to limit the amount of tar in the product gas.

- First, the use of olivine combined with a ratio $P_{H_2}/P_{H_2O} > 1.5$ in the reactive gas atmosphere leads to a toluene conversion rate higher than 90%.
- For experiments with "sand + 3%" char and "olivine + 3% char", results indicated that a steam partial pressure of 0.4 bars gives rise to a rate of carbon containing tars in the product gas of about 30%.

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References

[1] Milnes TA, Evans RJ. Biomass gasifier "tars": their nature, formation, and conversion. National Renewable Energy Laboratory; 1998.
[2] Devi L, Ptasinski KJ, Janssen FJJG. A review of the primary measures for tar elimination in biomass gasification processes. Biomass Bioenergy 2003;24:125–40.
[3] Abu El-Rub Z, Bramer EA, Brem G. Review of catalysts for tar elimination in biomass gasification processes. Ind Eng Chem Res 2004;43:6911–9.
[4] Dayton D. A review of the literature on catalytic biomass tar destruction, Milestone Completion Report; 2002.
[5] Sutton D, Kelleher B, Ross JRH. Review of literature on catalysts for biomass gasification. Fuel Process Technol 2001;73:155–73.
[6] Corella J, Toledo JM, Padilla R. Olivine and dolomite as in-bed additive in biomass gasification with air in a fluidized bed reactor: which is better? Energy Fuels 2004;18:713–20.
[7] Simell P, Kurkela E, Ståhlberg P, Hepola J. Catalytic hot gas cleaning of gasification gas. Catal Today 1996;27:55–62.
[8] Rapagnà S, Jand N, Kiennemann A, Foscolo PU. Steam-gasification of biomass in a fluidized-bed of olivine particles. Biomass Bioenergy 2000;19:187–97.
[9] Olivares A, Aznar MP, Caballero MA, Gil J, Francés E, Corella J. Biomass gasification: produced gas upgrading by in-bed use of dolomite. Ind Eng Chem Res 1997;36:5220–6.
[10] Miccio F, Piriou B, Ruoppolo G, Chirone R. Biomass gasification in a catalytic fluidized bed reactor with beds of different materials. Chem Eng J 2009;154:369–74.
[11] de Andrés JM, Narros A, Rodríguez ME. Behaviour of dolomite, olivine and alumina as primary catalysts in air-steam gasification of sewage sludge. Fuel 2011;90:521–7.
[12] Koppatz S, Pfeifer C, Hofbauer H. Comparison of the performance behaviour of silica sand and olivine in a dual fluidized bed reactor system for steam gasification of biomass at pilot plant scale. Chem Eng J 2011;175:468–83.
[13] Christodoulou C, Grimekis D, Panopoulos KD, Pachatouridou EP, Iliopoulou EF, Kakaras E. Comparing calcined and un-treated olivine as bed materials for tar reduction in fluidized bed gasification. Fuel Process Technol 2014;124:275–85.
[14] Göransson K, Söderlind U, Engstrand P, Zhang W. An experimental study on catalytic bed materials in a biomass dual fluidized bed gasifier. Renewable Energy 2015;81:251–61.
[15] Erkiaga A, Lopez G, Amutio M, Bilbao J, Olazar M. Steam gasification of biomass in a conical spouted bed reactor with olivine and γ-alumina as primary catalysts. Fuel Process Technol 2013;116:292–9.
[16] Kuhn JN, Zhao Z, Felix LG, Slimane RB, Choi CW, Ozkan US. Olivine catalysts for methane- and tar-steam reforming. Appl Catal B 2008;81:14–26.
[17] Virginie M, Libs S, Courson C, Kiennemann A. Iron/olivine catalysts for tar reforming: comparison with nickel/olivine, in Zakopane 2008: Catalysis for environment: depollution, renewable energy and clean fuel; 2008.
[18] Morin M, Nitsch X, Pécate S, Hémati M. Tar conversion over olivine and sand in a fluidized bed reactor using toluene as model compound. Fuel 2017;209:25–34.
[19] Nitsch X, Commandré JM, Clavel P, Martin E, Valette J, Volle G. Conversion of phenol-based tars over olivine and sand in a biomass gasification atmosphere. Energy Fuels 2013;27:5459–65.
[20] Uddin MdA, Tsuda H, Wu S, Sasaoka E. Catalytic decomposition of biomass tars with iron oxide catalysts. Fuel 2008;87:451–9.
[21] Caballero MA, Aznar MP, Gil J, Martin JA, Francés E, Corella J. Commercial steam reforming catalysts to improve biomass gasification with steam-oxygen mixtures. 1. Hot gas upgrading by the catalytic reactor. Ind Eng Chem Res 1997;36:5227–39.
[22] Taralas G, Kontominas MG. Numerical modeling of tar species/VOC dissociation for clean and intelligent energy production. Energy Fuels 2005;19:87–93.
[23] Fuentes-Cano D, Gómez-Barea A, Nilsson S, Ollero P. Decomposition kinetics of model tar compounds over chars with different internal structure to model hot tar removal in biomass gasification. Chem Eng J 2013;228:1223–33.
[24] Hosokai S, Kumabe K, Ohshita M, Norinaga K, Li C-Z, Hayashi J-I. Mechanism of decomposition of aromatics over charcoal and necessary conditions for maintaining its activity. Fuel 2008;87:2914–22.
[25] Sueyasu T, Oike T, Mori A, Kudo S, Norinaga K, Hayashi J-I. Simultaneous steam reforming of tar and steam gasification of char from the pyrolysis of potassium-loaded woody biomass. Energy & Fuels 2012;26:199–208.
[26] Abu El-Rub Z. Biomass char as in-situ catalyst for tar removal in gasification systems PhD Thesis University of Twente; 2008.
[27] Abu El-Rub Z. Experimental comparison of biomass chars with other catalysts for tar reduction. Fuel 2008;87:2243–52.
[28] Hosokai S, Norinaga K, Kimura T, Nakano M, Li C-Z, Hayashi J-I. Reforming of volatiles from the biomass pyrolysis over charcoal in a sequence of coke deposition and steam gasification of coke. Energy & Fuels 2011;25:5387–93.
[29] Shen Y. Chars as carbonaceous adsorbents/catalysts for tar elimination during biomass pyrolysis or gasification. Renew Sustain Energy Rev 2015;43:281–95.
[30] Klinghoffer NB, Castaldi MJ, Nzihou A. Catalyst properties and catalytic performance of char from biomass gasification. Ind Eng Chem Res 2012;51:13113–22.
[31] Nitsch X, Commandré J-M, Valette J, Volle G, Martin E. Conversion of phenol-based tars over biomass char under H_2 and H_2O atmospheres. Energy Fuels 2014;28:6936–40.
[32] Morin M, Pécate S, Hémati M, Kara Y. Pyrolysis of biomass in a batch fluidized bed reactor: effect of the pyrolysis conditions and the nature of the biomass on the physicochemical properties and reactivity of the char. J Anal Appl Pyrol 2016;122:511–23.
[33] Dufour A, Celzard A, Ouartassi B, Broust F, Fierro V, Zoulalian A. Effect of micropores diffusion on kinetics of CH_4 decomposition over a wood-derived carbon catalyst. Appl Catal A 2009;360:120–5.
[34] de Sousa L. Gasification of wood, urban wastewood (Altholz) and other wastes in a fluidized bed reactor, PhD Thesis; 2001.
[35] Di Blasi C. Combustion and gasification rates of lignocellulosic chars. Prog Energy Combust Sci 2009;35:121–40.