

## Influence of the Effective Parameters on H<sub>2</sub>:CO Ratio of Syngas at Low-Temperature Gasification

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The current research study presents a comprehensive mathematical model of gasification to investigate and assess the influence of effective operating parameters on gasifier performance in the low-temperature operation, relying on a detailed kinetic scheme and a multi-scale and multi-phase gasification reactor model. Since the syngas produced from the gasification process would be used for the chemical production purposes (such as Methanol, DME, etc.), therefore, the ratio of H<sub>2</sub>:CO is selected for evaluation as a benchmark of effectiveness. Furthermore, the ratio of CO:CO<sub>2</sub> is considered as a scale of assessing index of the completion of the process in low-temperature operation regarding to gasification and combustion processes. The model is validated with experimental data from elsewhere. The remarkable aim of this activity is to analyse the effect of different parameters with respect to H<sub>2</sub>:CO ratio to improve and sustain the process in low-temperature conditions. The detailed and extended discussions of this objective are presented in further works of the authors.

### 1. Introduction

In general, gasification is defined as an endothermic chemical process occurring at temperatures greater than 900 K that breaks down the organic materials into gaseous species, i.e., syngas (H<sub>2</sub>, H<sub>2</sub>O, CO<sub>2</sub>, CO and CH<sub>4</sub>). The produced syngas can be used in various applications such as production of substitute natural gas, production of chemicals as ammonia, methanol, hydrogen; transformation into a liquid fuel, as a gaseous fuel for generation of electrical power and so on. Since biomass is one of the most promising feedstock capable to satisfy the increased demand for renewable energies, biofuels, and green chemicals (Cucek et al., 2010; Klimes et al., 2010; Lam et al., 2010, Vaccari et al., 2005), it is being more interesting to investigate and survey the operating conditions influencing its efficiency and energy saving. On the other hand, biomass conversion to bio-products is tough to be industrially scaled-up due to the complexity of chemical and transport phenomena as well as to be integrated with other renewable sources that can support energy and steam generation for the gasification process (Ravaghi-Ardebili, et al., 2013).

To sum up, the challenges to approach the less energy intensive processes encourage the objective of this research to investigate the effective parameters on efficiency of low-temperature gasification. Thanks to the elemental composition of the biomass and coal (Cao et al., 2008), the ratio of H<sub>2</sub>:CO is differently affected by the operating parameters in gasification processes. In order to this, the ratio of H<sub>2</sub>:CO has been selected as a benchmark of efficiency to evaluate for the purpose of applying produced syngas in methanol synthesis process. Although, low-temperature gasification process (600 - 800 K) would be remarkably significant to preserve the energy, it is restricted by the effect of temperature on the kinetics involved in gasification. Thus, it is necessary to compensate with the relative optimized operating conditions and parameters. In order to this, the work appraises the effect of the fuel elemental characteristics, pre-treatment of feedstock (drying) and the modelled reactor for the gasification. In addition, the ratio of CO:CO<sub>2</sub> is selected as a scale to measure the efficiency of the process and contemplate the competition of the gasification/combustion.

## 2. Kinetic Mechanism

Due to the complexity of the kinetics governed in the gasification process, gas-solid interactions of the phases, secondary gas phase reactions and transport phenomena involved in, a detailed kinetics scheme is needed both for pyrolysis and for the successive gas phase reactions. Since they are still unavailable even for major products released a detailed kinetic model is necessary for predicting the yield of the process (Ranzi et al., 2013). Moreover, the chemical mechanisms need to be integrated into the particle model accounting for the transport phenomena, which are critical in predicting the overall performance of reactor. Developing and integrating such kind of models is complex, as it was discussed earlier (Mettler et al. 2012). Therefore, it is crucial to consider the comprehensive mechanistic models capable of describing the transport phenomena and reaction kinetics for enhanced influence of biomass pyrolysis together with the integration of the multi-scale and multi-phase models at process scale and develop the novel process solutions. In order to this, the model proposed by Sommariva and co-workers, is applied in this activity to evaluate and peruse the objective of this study (Sommariva et al., 2011).

## 3. Low- Temperature Gasification

As it is well-known, biomass gasification is one of the favourable thermochemical processes to provide the sustainable conversion of biomass to bio-fuels, which conventionally occurs at the temperature range of 900 - 1400 K. Although, the operation at high temperature is beneficial to meet the optimal conversion, due to energy saving objectives, it might be significantly considerable to apply the low –temperature conditions. For this purpose, it is necessary to optimize the key operating parameters and conditions such as pre-treatment of the feedstock, operating and design conditions in order to improve the efficiency of the low-temperature process and preserve the sustainability of the process. In order to this, it has been tried to provide a general comparison of the objectives of the present study, a parametric study on operating conditions and characteristic of the fuel. Novel solutions including design improvements of gasifier and the preparation of the fuels for applying the low-temperature gasification are presented in further work of the authors. In addition, to validate the results, the model is confirmed with the experimental data presented by Cao and co-workers (Cao et al., 2008).

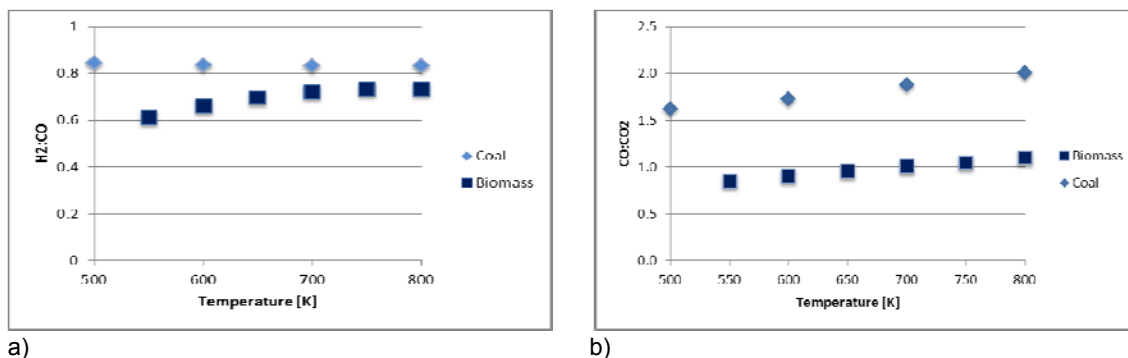
## 4. Adopted low-Temperature Gasifier

Updraft (moving bed) reactor configuration, also known as counter-current gasifier has been selected. Accordingly, in this configuration, feedstock is fed from the top of the reactor, and a grate at the bottom of the reactor supports the reacting bed. The gasifying agents (oxygen and steam) are introduced below the grate and diffuse up through the bed of biomass and char, while the product gases leave the reactor from the top of the reactor (Badeau, 2009). The agent entered from the bottom is in direct contact with hot ash at the bottom and unconverted chars dropping down. Therefore, the elevated temperature of wall at the bottom increases the ignition temperature of carbon. After providing the primary reactions and preheating in the start-up policy, the temperature of the gasification is dropped into the possible lowest temperature (e.g., from 1100 K to 700 K). Although the temperature of solar driven steam for gasification (Ravaghi-Ardebili et al., 2013) is lower (700 - 800 K) than the traditional one (900 - 1400 K), the various effective operating and pre-treatment parameters are adjusted to cover the objectives of the reliable energy saving through the process to cope with the deficiency caused by low temperature.

## 5. Results and Discussion

### 5.1 The effect of temperature on gasification

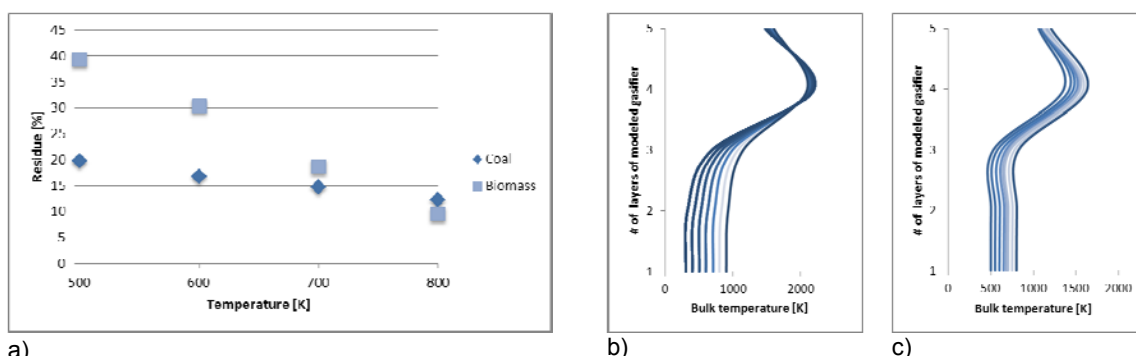
Under the designated conditions including the pre-treatment of feedstock (moisture percentage, particle size and component of feedstock), and operating conditions (steam to biomass ratio, equivalence ratio and size of the reactor), the temperature profile of low-temperature gasification is presented in Figure 1. These profiles display the efficiency of the low-temperature process in terms of  $H_2:CO$  and  $CO:CO_2$  ratios. As it is shown, due to the structure of biomass, the amount of gas produced in gasification and the ratio of  $H_2:CO$  varies between 0.6 - 0.78, whereas it is merely constant for coal (Figure 1.a). In addition, the evaluation of the competition between gasification and combustion, it is realized that the effectiveness of the process for coal in comparison with biomass considering the ratio of  $CO:CO_2$  (Figure 1.b).



a) b)  
Figure 1. The influence of low-temperature gasification on efficiency of process: a) H<sub>2</sub>:CO ratio, and b) CO:CO<sub>2</sub> ratio.

## 5.2 The effect of gas (bulk) temperature on gasification

This section considers the role of bulk temperature on the efficiency of the process. The profile of the temperature is investigated along the reactor under the axial-discretized reactor layers. The results are presented in terms of residue percentage in the solid stream escaped from the bottom of the gasifier (composed of ashes and unconverted solid fuel). Figure 2.a demonstrates that for the reliable process, gas temperature should be selected higher than 700 K, in order to obtain a reasonably low content of the solid residue in production (approximately 10-15 %) to declare the concern of energy saving. Moreover, the temperature profiles of gas along the layers of the gasifier (Figures 2.b, c) represent the results of the interaction of the gas and solid particles to exchange the heat.



a) b) c)  
Figure 2. a) The influence of low-temperature gasification on residue percentage of produced gas, and the temperature profile of gas (bulk) through the layers of modelled gasifier: b) coal, c) biomass.

## 5.3 The effect of feedstock characteristic

The biomass and coal are different in component properties such as the proximate analysis (fixed carbon, volatile materials, ash content and moisture content), the ultimate analysis (amount of carbon, oxygen, hydrogen, sulphur, nitrogen, and other impurities), and the heating value. Volatile materials (organic matter) in biomass account for more than 70 wt.%, while in coal for the range of lignite to anthracite (with sub-bituminous and bituminous coals in between) are about 27% for lignin-rank, and about to an average 5%, for anthracitic rank. A noticeable difference between coal and biomass is the composition of the organic matter. Woody biomass contains almost 50 wt. % carbon, 45 wt. % oxygen, whereas coal contains 60-85 wt. % (depending on its rank) and 5-20 wt. % oxygen (Prins et al., 2007).

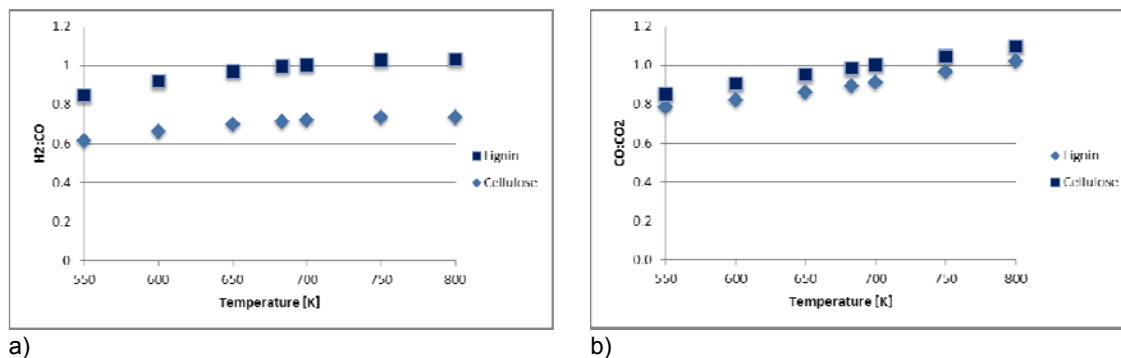
### 5.3.1 The Characterization of Biomass

Although the operating conditions may affect the throughput of the gasification, the composition of biomass influences the performance of the gasifier (Lede, 1999). A simplified description of biomass characterization is usually given in terms of proximate analysis (moisture, ash, fixed carbon, and volatile matters), elemental analysis (C, H, S, N, and O), or biochemical analysis (cellulose, hemicellulose, and lignin, together with extractives, in either water and ethanol or toluene) (Faravelli, et al., 2010). Relying on this, in this section, two different kinds of biomass are selected to investigate and evaluate the gasification performance (Table 1). The cellulose-based biomass is defined as a biomass with high content of cellulose and hemicellulose, whereas the lignin-based biomass is the biomass, so-called lignobiomass, with higher

Table 1. Composition (mass) of applied biomass (Ranzi et al., 2011).

Composition (%)	Cellulose	Hemicellulose	Lignin C	Lignin H	Lignin O	Ash
cellulose-based biomass	40	20	5	25	8	2
ligno-biomass	35	8	30	20	5	2

\*Lignin C, Lignin H and Lignin O represent their characteristic of being richer in carbon, hydrogen, and oxygen, respectively (Ranzi, et al., 2011).



a) Figure 3. The influence of biomass characterization on: a)  $H_2:CO$ , and b)  $CO:CO_2$  ratios.

content of lignin, derived from second-generation biomass conversion processes (e.g. second-generation bioethanol). Lignin-based biomass shows the greater effect on the proficiency of  $H_2:CO$  in comparison with the cellulose-based biomass (Figure 3.a). The higher content of carbon in lignin-based biomass yields the higher ratio of hydrogen production. The ratio of  $CO:CO_2$ , related to the competition between gasification and combustion processes, shows approximately an identical trend for the two above-discussed biomass components. Consequently, the proper selection of the physical and chemical parameters of the biomass feedstock is also crucial to improve the result of the low-temperature gasification.

### 5.3.2 The Characterization of Coal

The typical composition of Polish coal (Peterson, 2006) is considered to model and investigate (Table 2) the gasification process. The characterization of coal is pursued by a software (CHOSafer) in which, the ultimate analysis is given as input to define the characteristic of coal, which is defined as a mixture of three reference components called COAL1, COAL2 and COAL3. Figure 4 shows the output of the model in which, the triangle represents the percentage of hydrogen against the percentage of carbon (Sommariva et al., 2011).

Table 2. Ultimate analysis data of Polish coal (Peterson, 2006)

component	C	H	O	N	S
mass %	81.11	5.12	11.57	1.42	0.78

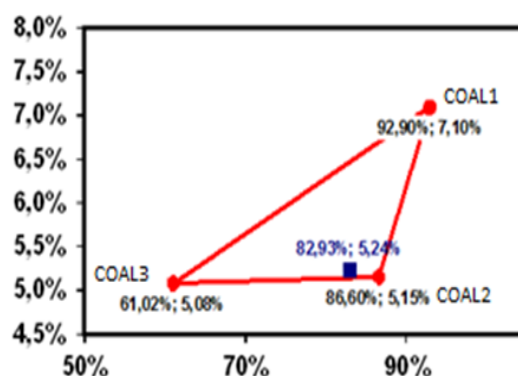


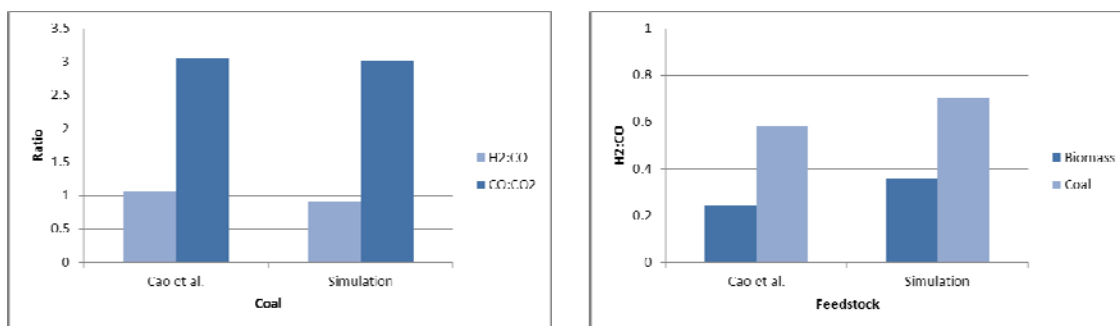
Figure 4. The selected COAL1, COAL2 and COAL3 in CHOSafer software (Sommariva, 2011).

The simulations of coal gasification are validated with the experimental data presented by Cao and co-workers (Cao et al. 2008). The results of the comparisons show a good agreement (Figure 5.a) for the

ratios of  $H_2:CO$  and  $CO:CO_2$ . Relying on this agreement, the simulation is then applied to compare the biomass and coal gasification, with special emphasis on the  $H_2:CO$  ratio (Figure 5.b).

Table 3. The characteristics of coal

	COAL1 [%]	COAL2 [%]	COAL3 [%]	Ash [%]	Water [%]
Cao et al. 2008	33.8	40.2	16.6	6.8	2.6
Simulation	31.35	46.87	13.9	5.9	2
	oxygen:coal ratio [Nm <sup>3</sup> /kg]		steam:coal ratio [kg/kg]		
Cao et al. 2008	0.314		0.8		
Simulation	0.431		0.81		



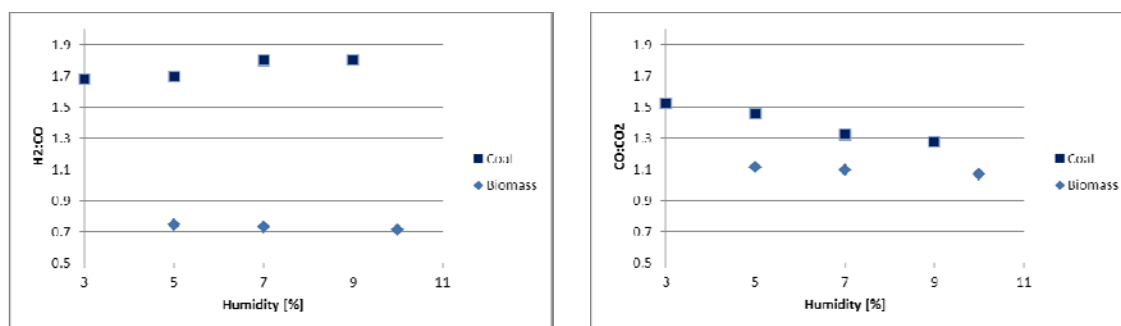
a)

b)

Figure 5. The influence of low-temperature gasification on efficiency: a) Coal, and b) comparison with experimental data.

#### 5.4 The effect of humidity

The moisture in the structure of the fuel has undesirable effect on gasification process. Since the high amount of moisture in fuel uses the energy and it results in decreasing the temperature of gasification, which determines an inefficient process. Biomass has high content of moisture in its structure in addition of other components. Therefore, it is necessary to reasonably decrease the content of water, especially in the case of low-temperature gasification. Thus, the pre-treatment process is required to dry the feedstock before feeding it into the gasifier. Although drying is an energy-intensive pre-treatment process, it provides considerable benefits for combustion and gasification compared to their initial raw state such as increased boiler efficiency, lower fuel gas emissions, and improved operations in utilities (Li et al., 2012; Gebreegziabher et al., 2013). The content of water in feedstock could affect the efficiency of the process and decrease the yield of produced syngas. Therefore, it needs to be pre-treated and dried before to be applied as feedstock (Figure 6).



a)

b)

Figure 6. The influence of humidity on efficiency of low-temperature gasification :a)  $H_2:CO$  and b)  $CO:CO_2$ .

## 6. Conclusions

The low-temperature gasification of biomass and coal was proposed in this work together with considerations on the effective parameters to enhance the efficiency of the process. The ratio of  $H_2:CO$  was assessed as a benchmark of efficiency due to the further application of syngas (i.e. methanol

synthesis). The work evaluated the feasibility of low-temperature gasification with respect to the modelled gasifier, feedstock characterization and humidity of fuel. In addition, validation of the applied model was accomplished by comparison with the experimental data of the literature and was in good agreement for both biomass and coal gasification. The full discussion on the low-temperature gasification, considering a broader range of effective parameters, is presented in further works of the authors.

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