

Kinetic Modeling of Supercritical Water Gasification: Preliminary Results

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The aim of this work is to model the supercritical water gasification (SCWG) of methanol by means of a detailed kinetic model based on elementary reactions. The challenge is represented by modeling SCWG by using the existing models developed for combustion or supercritical water oxidation (SCWO) and by varying their initial conditions to make them suitable for SCWG. To this purpose, three models (GRI-Mech 3.0, Brock and Savage and Webley) were selected, implemented in MatLab[®] environment and run. Webley's model seems to describe quite well methanol conversion as a function of time. On the other hand, some mechanisms, like water-gas shift and methanation, are not correctly predicted.

1. INTRODUCTION

Supercritical water gasification (SCWG) is one of the most promising technologies to convert biomass into a combustible gas, eventually rich in hydrogen, which can be used to produce electricity. This process can be particularly effective to treat wet biomasses, which could not be valorized otherwise [1]. Traditional air-based gasification processes, in fact, require high dried biomass, thus many residual materials could not be suitable for such treatment. Moreover, state-of-art gasification techniques cause the formation of undesired compounds, such as tars and char. These substances, which are non-equilibrium compounds, are extremely problematic, since they can cause reactor fouling and plugging, as well as damages to the mechanical parts of engines and turbines [2].

Supercritical water gasification is able to overcome these problems. SCWG is based on the usage of supercritical water as gasifying agent, that is water above its critical point (temperature and pressure higher than 375°C and 221 bar). Under these conditions, water exhibits properties which are halfway between a liquid and a gas, with high density but also low viscosity and high diffusivity. Furthermore, the behavior of supercritical water is even more unique. When supercritical conditions are achieved, water changes its nature from a polar compound to an almost non-polar substance [3]. This makes water able to solvate many organic substances, including those responsible for the formation of char and tar (mainly polycyclic aromatic hydrocarbons). As a results, many experiments of SCWG show nearly no formation of char and tars [4-5].

Only a few works have been presented on the mathematical modeling of SCWG. Nearly all the efforts have been dedicated to thermodynamic modeling [6-7]. This approach is able to predict the equilibrium composition of a system; in other words, a thermodynamic model tells which is the system composition after a very long time. This approach is useful to gather important information about the influence of the main process parameters (temperature, pressure, biomass composition and concentration) and also to perform energy calculations to determine the process heat duty [8-9]. On the other hand, thermodynamic modeling gives no

information about the transient state, where intermediate compounds are formed. Moreover, such approach is not useful for reactor sizing and design, since it does not account for the time required by each process to develop. All these aims could be achieved by means of a kinetic model.

The aim of this work is to apply the same elementary reaction models originally conceived for supercritical water oxidation (SCWO) and combustion to the case of the SCWG of methanol, which can be considered as a model compound for real biomass. Such approach is completely new in the state-of-art literature. Three different models were chosen, implemented and then run. The models were also compared to literature experimental data.

2. THEORY

Each kinetic model is composed of a certain number j of components, i.e. chemical species, and a certain number i of elementary reactions. An elementary reaction describes the actual physical event leading to the transformation of the reagents into the products and, consequently, normally involves a limited number of molecules (in general one or two). For example, for the generic i -th elementary reaction:



The net reaction rate r_i can be expressed as the difference between forward and backward reaction rates:

$$r_i = k_i C_A^\alpha C_B^\beta - k_{-i} C_C^\gamma C_D^\delta \quad (2)$$

Where the term k_i is the kinetic constant of the forward reaction, k_{-i} is that of the backward one and C_j is the molar concentration of the specie j . The forward reaction kinetic constant can be calculated through the modified Arrhenius expression:

$$k_i = k_{o,i} T^{n_i} \exp\left(-\frac{E_{act,i}}{RT}\right) \quad (3)$$

Where $k_{o,i}$ is the pre-exponential factor, n_i is an exponent for the dependence on the temperature T , $E_{act,i}$ is the reaction activation energy and R is the universal gas constant.

Following this procedure, all the forward reaction rates can be calculated. To calculate the backward ones, it is possible to use thermodynamic consideration. At thermodynamic equilibrium, in fact, the rate of forward and backward reactions are equal. As a consequence, for the generic reaction i :

$$k_i C_A^\alpha C_B^\beta = k_{-i} C_C^\gamma C_D^\delta \quad (4)$$

Thus:

$$\frac{k_i}{k_{-i}} = \frac{C_C^\gamma C_D^\delta}{C_A^\alpha C_B^\beta} = \prod_j C_j^{\nu_{j,i}} = Q_i \quad (5)$$

Where $\nu_{j,i}$ is the stoichiometric coefficient of the component j in the reaction i . The term Q_i is called reaction quotient and it represents the ratio between the concentrations of reactants and products at equilibrium, each elevated to its own stoichiometric coefficient. This quantity can be related to the equilibrium constant $k_{eq,i}$ of the reaction, which can be defined as:

$$k_{eq,i} = \exp\left(-\frac{\Delta G^o}{RT}\right) = \prod_j a_j^{\nu_{j,i}} \quad (6)$$

Where the term ΔG^o is the difference of Gibbs free energy between products and reactants at reference pressure (101,325 Pa) and a_j is the activity of the specie j , that is:

$$a_j = \frac{P\phi_j x_j}{P_o} \quad (7)$$

Where P is the system pressure, P_o is the reference pressure, ϕ_j and x_j are respectively the fugacity coefficient and the molar fraction of the j -th specie. If all the species are assumed to behave as ideal gases, ϕ_j is equal to 1. Moreover, the equation of state for ideal gases and the Dalton's law allow to write:

$$C_j = \frac{n_j}{V} = \frac{Px_j}{RT} \quad (8)$$

Substituting equation 8 into equation 5:

$$Q_i = \prod_j C_j^{\nu_{j,i}} = \left(\frac{P_o}{RT}\right)^{\sum_j \nu_{j,i}} \exp\left(-\frac{\Delta G^o}{RT}\right) \quad (9)$$

Thus, the kinetic constant for the reverse reaction is straightly determined as:

$$k_{-i} = \frac{k_i}{Q_i} \quad (10)$$

Some reactions in the model show pressure-dependent rates. These reactions are often represented by dissociation reactions and they are modeled following the Lindemann's approach. The kinetic constant for such reactions can be expressed by:

$$k = F \frac{k_0 k_\infty C_M}{k_0 C_M + k_\infty} \quad (11)$$

Where k_0 and k_∞ are at their turn two kinetic constants that depend on the temperature through an Arrhenius-like relation. F is called "broadening parameter", it is derived through RRKM calculations and it depends on the temperature, too. M is a generic specie in the system.

The reactions are assumed to happen in an isobaric batch reactor, that is a discontinuous reactor whose volume can vary in order to keep the pressure constant. In such system, the mass balance for the j -th component gives:

$$\frac{dC_j}{dt} = \sum_{i=1} \nu_{j,i} r_i - \frac{C_j}{V} \frac{dV}{dt} \quad (12)$$

The time derivative of the reactor volume V can be calculated from a mass balance on the sum of all components, recalling that in an isobaric system the total concentration C_T is constant:

$$\frac{dV}{dt} = \frac{V r_T}{C_T} \quad (13)$$

Where r_T is the sum of all the reaction rates. The expression of the mass balance for the j -th component thus becomes:

$$\frac{dC_j}{dt} = \sum_{i=1} \nu_{j,i} r_i - \frac{C_j r_T}{C_T} \quad (14)$$

The model output is then the solution of the system of j non-linear ODEs in the form of 14. To perform the calculations, a set of initial conditions must be chosen, which are the concentration of each specie at time zero.

3. OVERVIEW OF THE MODELS AND IMPLEMENTATION

In the present work, three different models were analyzed. Each of them involves a certain number of components, i.e. the chemical species, and a certain number of reactions. All the models give a set of kinetic parameters: for each reaction, k_o , n and E_{act} are given for the forward reactions. Reverse reaction rates are calculated in the way described in Section 2.

The three models which were chosen for the analyses are GRI-Mech 3.0 [10], Brock and Savage's model [11] and Webley's model [12]. Each of these models accounts for gas-phase radical mechanisms. Radical reactions can be assumed to be the only reactions that take place in supercritical water at high temperature and pressure. At such conditions, the ionic product of water is extremely low, thus ionic reactions can be reasonably ignored [11].

GRI-Mech 3.0 [10] is a model developed to describe the combustion of air/methane mixtures; however, its application can be also extended to the combustion of other light hydrocarbons. In its original form, it consists of 325 reactions and 53 components. However, since many reactions are intended to describe the formation of nitrogen compounds in combustion reactions, which are not of interest in the present work, a subset of the model was considered. Such subset consists of 215 reactions and 34 components.

Brock and Savage's model [11] was conceived for the supercritical water oxidation of methane, hydrogen and C₁ compounds. It is based on 148 reactions with 22 components. All the elementary reactions were taken from existing literature data about combustion and atmospheric chemistry.

Webley's model was also developed for methane and methanol SCWO, but it can also account for the presence of ammonia and other nitrogen compounds [12]. Such mechanism foresees 88 elementary reactions with 24 components. However, since in this work N-compounds are neglected, a subset of 66 reactions and 17 components was considered. As well as Brock and Savage, model parameters were taken from the existing chemical kinetics literature.

It is worth noticing that neither Brock and Savage's nor Webley's models were calibrated by their authors to better fit experimental data. On the other hand, GRI-Mech 3.0 was optimized for CH₄ combustion, thus its reliability can be questionable outside its standard application field.

The models were implemented by means of the computing package MatLab[®]. Thermodynamic data were taken from NASA polynomials [13]. The resulting system of ODEs results in a stiff problem, which was solved through the routine ODE15S, which can deal effectively with this kind of numerical problems. Among the initial conditions, the total molar concentration C_T was calculated through Peng-Robinson equation of state.

The three models were run at a temperature of 600°C and a pressure of 250 bar, with a methanol concentration of 50% on a weight basis, corresponding to 36% on a molar basis. These conditions are the same of the experimental work of Boukis *et al.* [14], who gasified methanol in supercritical water by means of a reactor made of nickel-based alloys. A comparison between model outputs and experimental results was established.

4. RESULTS AND DISCUSSION

First of all, each model was run in order to assess its specific behavior. Then a comparison on methanol conversion rate and principal gaseous products production was established.

4.1 Model runs

Figure 1 shows the model results obtained by means of GRI-Mech 3.0. The results exhibit a quite slow reactions, that take place in a long time scale. Among the products, only H_2 and CO are present in significant amounts; formaldehyde is also present as a reaction intermediate in the first seconds.

The steady-state which is achieved is represented by the dissociation reaction of methanol into two moles of hydrogen and one mole of carbon monoxide. Water has nearly no role in the reaction mechanism.

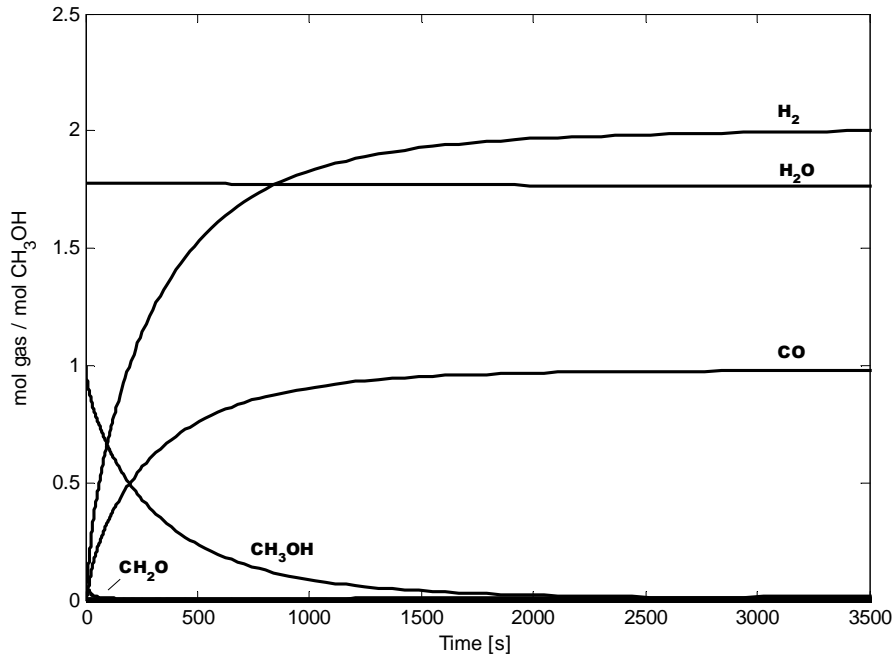


Figure 1 – Product gas composition predicted by GRI-Mech 3.0 kinetic model.

Figure 2 shows the same analysis made for Brock and Savage's model. First of all, faster kinetics can be seen: the system reaches its steady state just after 150 s. Here, among the reaction products, methane is also present.

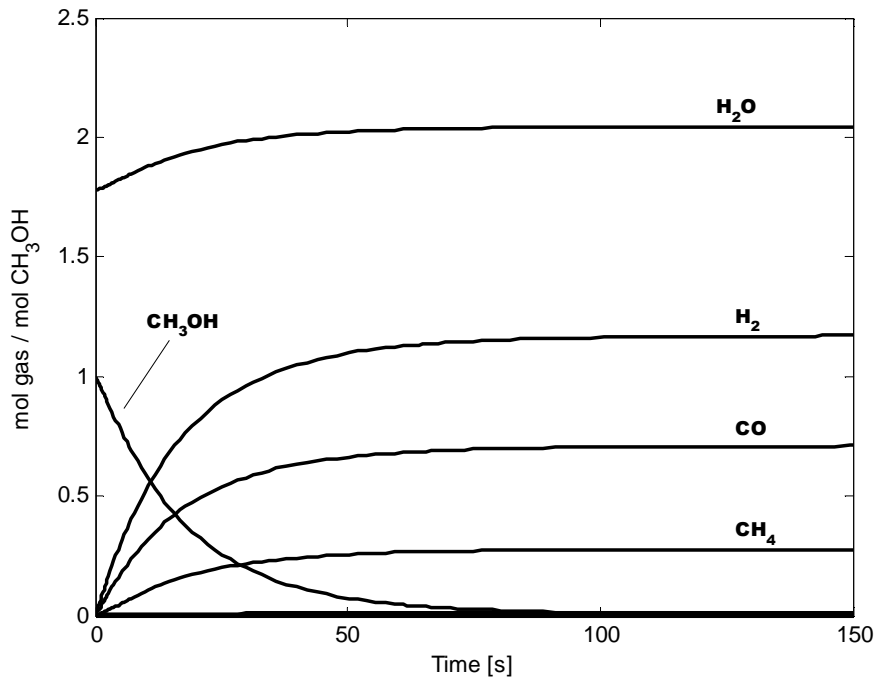


Figure 2 – Product gas composition predicted by Brock and Savage’s kinetic model.

Furthermore, it is possible to notice that water increases during the first seconds of run. A more detailed analysis of the reaction mechanism revealed that water increase is related to methane formation, owing to the following mechanism:



Again, water does not participate in the reaction; in this case it is even a product. As a consequence of methane formation, H₂ and CO yields are lower with respect to the GRI-Mech 3.0.

Figure 3 shows the results of the analysis for Webley’s model. For this representation, two time scales were adopted, since some important phenomena take place in the first seconds of reaction, while other ones can be appreciated only with long-term runs.

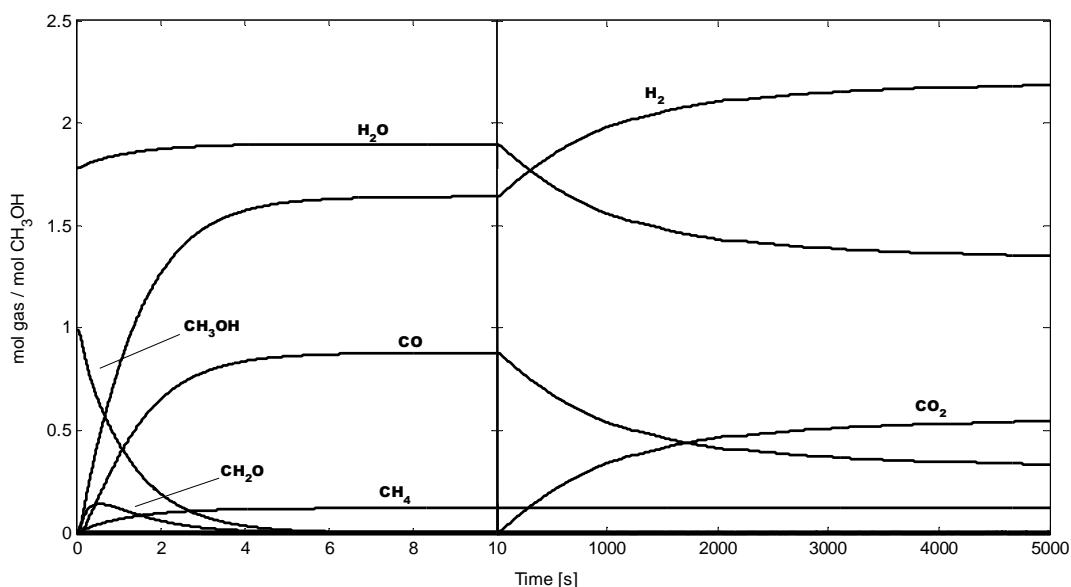


Figure 3 – Product gas composition predicted by Webley's kinetic model.

In Webley's model, methanol decomposition kinetics is definitely faster and a complete conversion is achieved in less than 6 seconds. Water exhibits a behavior similar to that described above: it acts as a reaction product, since it is produced along with the formation of methane (eq. 15-16). Formaldehyde formation is also clearly visible in the first seconds of reaction. This chemical specie shows a peak and then it is completely consumed.

After some seconds, a sort of steady state seems to be reached. Anyway, if a simulation is performed for longer times, the effect of water-gas shift reaction can be clearly seen. This reaction converts water and carbon monoxide into hydrogen and carbon dioxide, as it can be seen in the right portion of Figure 3. Methane is not involved in long-term reactions.

4.2 Methanol conversion

A first comparison among the models was made by comparing methanol conversion, that is the ratio between the mass of the reacted methanol and its initial amount. The results of this comparison are shown in Figure 4.

Methanol conversion rates are quite different for each model. Webley's model seems to fit the experimental data quite well, foreseeing an almost complete methanol conversion in the first 10 seconds. The other models show slower kinetics. GRI-Mech mechanism is the slowest: in the first 10 seconds, it foresees a conversion lower than 10%.

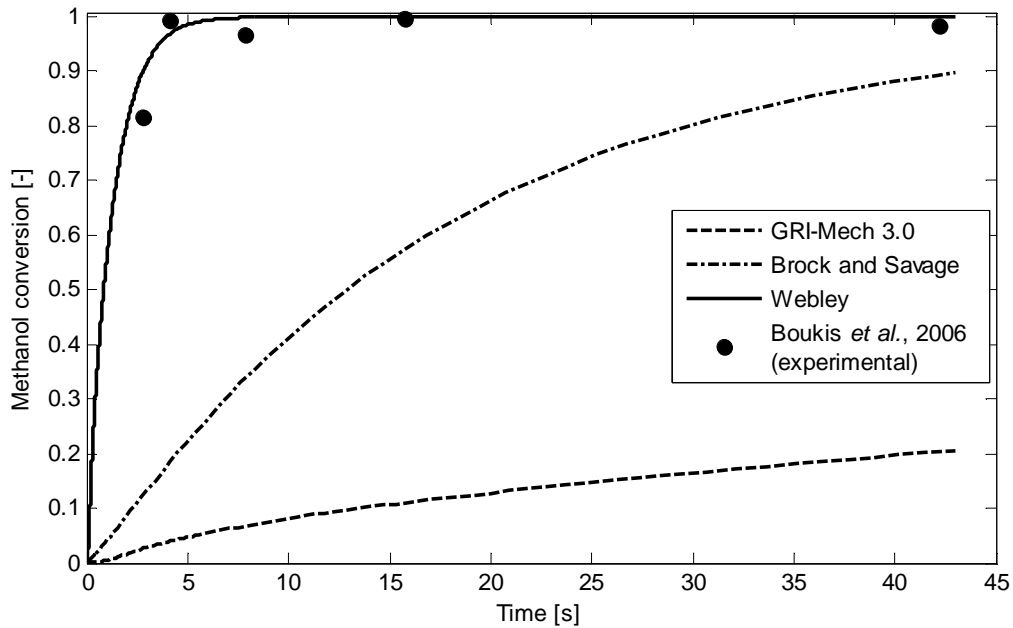


Figure 4 – Methanol conversion: comparison between models and experimental results.

These results can be explained by analyzing the structures of each model. GRI-Mech, which was thought to deal with methane combustion, was optimized for high temperature reactions. Moreover, some important reaction for methanol are not foreseen.

Models by Brock and Savage and Webley present nearly the same key-reactions. However, they use a different approach to pressure-dependent reactions. In Webley's model, all the possible pressure-dependent reaction are assumed to take place at their high pressure limit, thus having first-order kinetics. This is not always true in Brock and Savage's approach, where the same reactions have reaction orders between 1 and 2, with generally slower rates.

Owing to these results, it was chosen to restrict any other comparison to the sole Webley's model, since the other ones exhibit too different responses with respect to the experimental data.

4.3 Product gas composition

The comparison between the product gas composition predicted by Webley's model and the experimental findings of [14] is presented in Figure 5.

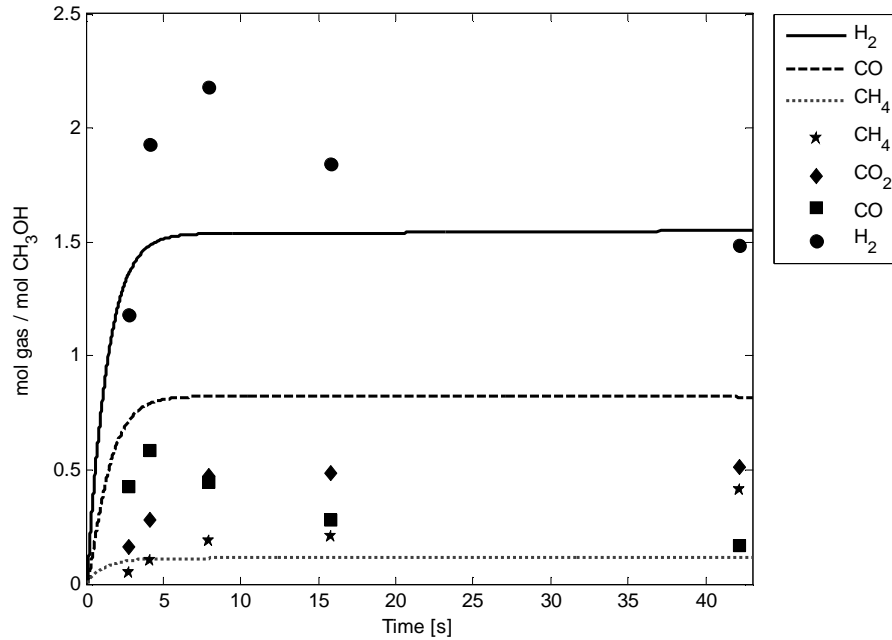
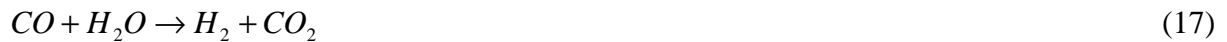


Figure 5 – Comparison between Webley's model results (lines) and experimental data by [14] (points).

Though the model is able to foresee the methanol decomposition rate in a very effective way, product gas composition is not predicted with the same accuracy. The experimental data, in fact, show that hydrogen has a peak at around 10 seconds and then it decreases. A similar behavior is that of carbon monoxide, while methane and carbon dioxide show a monotonic increasing trend.

Webley's model does not succeed in forecasting these trends. It generally overestimates CO, and H₂ peak is not present. Methane is well described only up to 5 seconds, then the model underestimates its production. Carbon dioxide is completely absent in the model results.

A possible explanation for the experimental trend can be the presence of two important reactions: water-gas shift (WGS) and methanation. Water-gas shift converts CO and H₂O into H₂ and CO₂:



Methanation reaction converts CO and H₂ into CH₄ and H₂O:



Both reactions 17 and 18 normally take place through catalytic mechanisms, where a metallic surface is involved. During experimental activities, the metallic surface is usually represented by the reactor walls, which many authors say to exert a significant influence on kinetics [15]. Since the implemented model is developed for homogeneous gas-phase reactions, it is not able to model reactions 17 and 18. As a consequence, the sole methanol decomposition to CO, H₂ and a few CH₄ is predicted.

The fact the model results fit the methanol decomposition experimental data in a good way may suggest that CH₃OH decomposition reactions actually take place in a gaseous

homogeneous phase. On the other hand, the other reactions, through which the gaseous species rearrange themselves to give the final equilibrium products, are most likely to happen on the surface of a catalyst. An extension of the model with such heterogeneous reactions should help to obtain better results.

5. CONCLUSIONS

In the present work, three different models were implemented to describe methanol gasification in supercritical water. Model results were also compared with experimental data. Though the different models are based nearly on the same set of key reactions, their results are very different. Only Webley's model seems to interpret the experimental data in a satisfactory way.

A common characteristic between the three models is the fact they predict methanol decomposition to simpler molecules but they do not describe any interaction with water. Water, in fact, acts like an inert and, in some cases, even as a product. Only in the long-term behavior, homogeneous-phase water-gas shift reaction is predicted.

These results suggest that probably, in real life water-gas shift and methanation take place on the surface of a catalyst (i.e. the reactor walls), and thus a simple homogeneous phase model like the one presented in this work is not able to describe them. Future work will consist in adding catalytic kinetics to the present models in order to achieve better results.

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