



Use of CO₂ as a co-reactant to promote syngas production in supercritical water gasification of sugarcane bagasse



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ABSTRACT

In this paper, thermodynamic equilibrium approaches are used to study the effect of CO₂ addition, as co-reactant in supercritical water gasification (SCWG) of sugarcane bagasse to improve syngas production. The effects of temperature, pressure, biomass composition and co-reactant composition were evaluated under equilibrium compositions for isothermic systems and thermal behavior for adiabatic systems. The CO₂ concentration in feed was analyzed at three different mass compositions: 15, 25 and 35 (wt%). The Virial equation of state was used to represent the non-ideality of both isothermic and adiabatic systems. The problems were formulated as optimization problems (non-linear programming) and the software GAMS with the CONOPT solver were used to solve them. Syngas with a H₂/CO molar ratio close to 2 (ideal for further Fischer–Tropsch synthesis application) was obtained with an addition of CO₂ as a co-reactant at 35 wt%. The calculated final temperatures were close to the initial ones, indicating low energy requirements for maintain these reactions.

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1. Introduction

Gasification is a process in which solid or liquid carbonaceous materials, such as biomass, react with water (steam), oxygen or air, to produce a gas containing carbon monoxide (CO), carbon dioxide (CO₂), hydrogen (H₂) and methane (CH₄) in different proportions, this gas is commonly named as syngas. Different papers emphasize that gasification reactions occurs by a complex combination of reactions in solid, liquid and gas phases, these reactions includes the pyrolysis, partial oxidation and steam reforming [1–3].

Generally, the conventional gasification process is carried out at high temperatures (700–1000 °C) and atmospheric pressure. The gas product can be used in different processes depending on the obtained composition [4]. But the convectional gasification processes presents a significant drawback, the feedstock needs to be dry enough, with a high-energy expenditure, to ensure a high conversion efficiency in conventional gasification process.

As an alternative to conventional gasification processes, appears the gasification of biomass in supercritical water (SCW) ($T_C \geq 374$ °C) and ($P_C \geq 22.1$ MPa) in this process there is no need to reduce the moisture content prior to the gasification process, because water is used as a medium to provide the desired operating condition in the process [4]. Therefore, for wet substrates, like as

biomass, containing large amounts of water, supercritical water gasification (SCWG) appears as a suitable technology [5].

The SCWG is related to present large hydrogen yields, but the excess of water inhibits the CO production in the system and thus, the production of syngas with a useful H₂/CO molar ratio is very low. The use of co-reactants appears as a strategy to promote syngas production in SCWG processes [6,7].

CO₂ utilization technologies have merged in recent years to reduce CO₂ emissions and developing beneficial uses of CO₂ [8]. The catalytic conversion of CO₂ to liquid fuels is a critical goal that would positively affect the global carbon balance by recycling CO₂ into energy for consumption.

Among many sources of biomass, sugarcane bagasse appears as an interesting biomass source for biofuel production, especially in Brazil. It contains about 50% cellulose, 25% hemicellulose and 25% lignin (in weight basis, wt%) in its composition. Due to its abundant availability, it can serve as an ideal substrate for microbial processes as well as energy conversion via combustion or gasification for the production of fuels and value added gases [9].

In this paper, thermodynamic equilibrium approaches are used to study the use of CO₂ as co-reactant to promote syngas production in SCWG of sugarcane bagasse. The effects of temperature, pressure, biomass composition and co-reactant composition were evaluated under equilibrium compositions and thermal behavior for isothermic (using Gibbs energy minimization method) and adiabatic (using entropy maximization method) systems. Both problems were formulated as optimization problems (non-linear

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Nomenclature

a_{mi}	number of atoms of element m for component i
B	second virial coefficient
B_{ij}	cross second virial coefficient
Cp_i	heat capacity of pure component i
G	Gibbs energy
H_i	partial molar enthalpy of component i
n_i^k	number of moles of component i in the phase k
n_i^0	initial number of moles of component i
$n_{C(s)}^s$	number of moles of solid carbon in solid phase
P	pressure
P_C	critical pressure
R	universal gas constant
SCWG	supercritical water gasification
T	temperature
T_C	critical temperature
V_C	critical volume
y_i	molar fraction of component i

Superscripts

g	gas phase
l	liquid phase
s	solid phase

Subscripts

i	refers to component i
m	refers to element m in a component

Greek symbols

μ	chemical potential
μ_i^0	chemical potential of component i at reference condition
$\mu_{C(s)}^0$	chemical potential of solid carbon at reference condition
ϕ_i	fugacity coefficient of component i
$\hat{\phi}_i$	fugacity coefficient of component i in the mixture
ω	acentric factor

programming) and the software GAMS in combination with CONOPT solver, were used to solve them.

2. Methodology

2.1. Thermodynamic modeling for isothermic systems

The equilibrium state to a closed system can be defined as the state in which the total Gibbs energy is at a minimum with respect to all possible changes at constant pressure and temperature. For a given temperature, pressure and inlet composition, the total Gibbs energy of the system has to be minimized to reach the equilibrium state:

$$G = \sum n_i^k \mu_i^k \quad (1)$$

For a given multiphase system, considering the problem can be formulated as an optimization problem, considering the formation of a gas and one solid phase, Eq. (1) can be rewritten as:

$$\min G = \sum_{i=1}^{NC} n_i^g \mu_i^g + \sum_{i=1}^{NC} n_i^s \mu_i^s \quad (2)$$

While satisfying the restrictions of non-negative number of moles of each component in each phase:

$$n_i^g, n_i^l, n_i^s \geq 0 \quad (3)$$

In addition, the restriction of mole balances, given by atom balance for reactive systems (non-stoichiometric formulation):

$$\sum_{i=1}^{NC} a_{mi} \cdot (n_i^g + n_i^l + n_i^s) = \sum_{i=1}^{NC} a_{mi} \cdot n_i^0 \quad m = 1, \dots, NE \quad (4)$$

The values of μ_i^g can be calculated from the formation values given at some reference conditions, using the following thermodynamic conditions:

$$\left(\frac{\partial H_i}{\partial T} \right) = Cp_i \quad i = 1, \dots, NC \quad (5)$$

$$\frac{\partial}{\partial T} \left(\frac{\mu_i}{RT} \right)_P = - \frac{H_i}{R \cdot T^2} \quad i = 1, \dots, NC \quad (6)$$

In this work, which considers only a gas phase and a possible solid phase as carbon for coke formation, the Gibbs energy can be expressed as:

$$G = \sum_{i=1}^{NC} \mu_i^0 + RT(\ln P + y_i + \ln \phi_i) + \sum_{i=1}^{NC} n_{C(s)}^s \mu_{C(s)}^0 \quad (7)$$

2.2. Thermodynamic modeling for adiabatic systems

The thermodynamic equilibrium condition for reactive multi-component closed systems, at constant P and enthalpy (H), with given initial composition, can be obtained by maximization of the entropy (S) of the system, with respect to n_i^k :

$$\max S = \sum_{i=1}^{NC} n_i^g S_i^g + \sum_{i=1}^{NC} n_i^l S_i^l + \sum_{i=1}^{NC} n_i^s S_i^s \quad (8)$$

While satisfying the same previous restrictions, given by Eqs. (3) and (4). Usually, physical properties are given as functions of composition, pressure and temperature, not enthalpy. Therefore, an additional restriction, referent to enthalpy balance, must be satisfied:

$$\sum_{i=1}^{NC} (n_i^g H_i^g + n_i^l H_i^l + n_i^s H_i^s) = \sum_{i=1}^{NC} (n_i^0 H_i^0) = H^0 \quad (9)$$

The entropy of each component in the mixture and the enthalpy balance can be determined using the following thermodynamic relations:

$$S_i^k = - \left(\frac{\partial \mu_i^k}{\partial T} \right)_{P, n_i^k} \quad i = 1, \dots, NC \quad (10)$$

$$\frac{H_i^k}{T^2} = - \frac{\partial}{\partial T} \left(\frac{\mu_i^k}{T} \right)_{P, n_i^k} \quad i = 1, \dots, NC \quad (11)$$

The absence of liquid phase and the presence of solid carbon as pure component were considered to build this model. The entropy was determined using the chemical potential of each component in the mixture and the chemical potential can be determined using the previous presented Eqs. (5) and (6). So the total entropy can be expressed as follows:

$$S = \sum_{i=1}^{NC} n_i^g \left(S_i^{g0} - R \left(\ln P + \ln \phi_i + \left(\ln n_i^g - \ln \sum_{j=1}^{NC} n_j^g \right) \right) \right) + \sum_{i=1}^{NC} n_i^s S_i^{s0} \quad (12)$$

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