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DFT and canonical ensemble investigations on the thermodynamic properties of Syngas and natural gas/Syngas mixtures

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ABSTRACT

Density Functional Theory and canonical ensemble were used to investigate thermodynamic properties of Syngas and its mixture with natural gas. The following thermodynamic potentials were obtained: internal energy, enthalpy, entropy and Gibbs free energy for temperatures ranging from 0.5 K to 1500 K. It was observed that CO and H_2 were the most stable Syngas components, possessing the ability to render Syngas less favorable to the temperature increase. Also, we verified that Syngas presents properties similar to an antiknock agent for natural gas, raising its resistance to temperature increases. Were determined the Poisson coefficients and Bulk modulus for Natural gas/Syngas mixtures and Shomate equation coefficients for some Syngas types, providing a more complete thermodynamic description for these gases. Additionally, thermodynamic potentials of combustion for Natural gas/Syngas mixtures were predicted, showing that this biofuel can reduce the calorific power of natural gas and makes its combustion less favorable due its antiknock behavior. However, a mixture with 30% of Syngas may be useful for natural gas combustion, since it present a calorific power between 73.41% and 79.49% of that of natural gas, which is a substantial fraction of energy released during combustion, showing good future prospects to the Natural gas/Syngas mixture to the renewable energy generation.

1. Introduction

The combining of fossil fuels with biofuels is becoming common practice in the most diverse sectors of industry around the world, and principally in the automotive sector [1]. This is due to the non-renewable character of fossil fuels, as well as their environmental drawbacks, like their emission of polluting gases into the atmosphere [1–4]. Some examples of these mixtures are ethanol-gasoline [5–7], kerosene-biokerosene [8,9] and diesel-biodiesel blends [10,11].

However, another proposal for fuel which incorporates this kind of blend points to natural gas (NG) combined with a synthesis gas (Syngas), which is a biogas produced from biomass gasification [12–14], a technique that converts a solid biomass into a combustible gas. Thus, since the composition of Syngas contains lighter molecules (H_2, CO, CH_4, …) [15–19], this biofuel has characteristics similar to NG. Consequently, recent studies have been developed which have aimed to use Syngas as a complement to the composition of other fuels, such as NG, in internal combustion engines [20–23].

Hagos et al. [20]compared the performance of Syngas and NG during the direct injection stage in spark ignition engines, noting that in this stage Syngas is capable of supporting higher cylinder pressures than NG, being more stable and presenting a greater rate of heat release during combustion.

Johansson et al. [21] performed some tests with Syngas and NG in a system for chemical-looping combustion (CLC), in order to compare the conversion of these fuels due to combustion when interacting with oxygen-carriers. This system was operated successfully, presenting a good gas conversion rate. They observed a conversion around 99% for the Syngas and for the NG. With regard to Syngas, the final amounts of hydrogen and carbon monoxide

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were 1.8% and 2%, while for NG the methane fraction was between 0.5 and 1.5%.

Donohoe et al. [22] presented a study on the influence of steam dilution on the autoignition of some gases; as in, for example, the Syngas and natural gas mixtures under gas turbine-relevant conditions. Throughout the experiments, machine rapid compression was carried out for fuel/air mixtures. However, it was observed that significant changes in the thermal properties of the mixtures had an effect on their reactivity.

Le Cong et al. [23] performed an experimental study on the oxidation of methane-based fuels in the presence of Syngas. From this investigation, a detailed chemical kinetic model was produced, yielding a good agreement with the empirical data, such as in the burning velocities.

The greater stability of Syngas indicates that it has antiknock characteristics, which can be highly important for better engine performance [24]. In a review by Boehman and Le Corre [25] this importance was demonstrated in their investigation on the capacity of Syngas to raise the combustion temperature of some fuels, increasing their efficiency and optimizing their combustion [26].

Despite its great relevance on issues related to the use of biomasses for the generation of energy, until recently few studies have reported on a thermodynamic analysis of an NG/Syngas mixture. These results are to a large extent useful in contributing to a better understanding of the antiknock properties of Syngas, and of the other effects associated with the addition of Syngas to NG. Therefore, the present work aims to show a recommended DFT method, for predicting some of the thermodynamic properties of Syngas and the NG/Syngas blend as a function of any useful temperature and for their combustion properties. Additionally, these amounts correspond to properties calculated for several quantities of Syngas fractions, providing greater knowledge about the effect of Syngas when it is combined with NG, as for example, its ability to act as an antiknock agent for NG, which could be observed through this study. For this investigation, two models were adopted, the Density Functional Theory (DFT) [27,28], which is a sophisticated model based on quantum mechanics, and the canonical ensemble model of statistical thermodynamics [29].

2. Methodology

The simulations performed in this research describe the thermodynamic properties of nine kinds of Syngas from different biomasses and/or different gasification conditions [15–18]. The pressure and temperature conditions, under which the calculations were performed, are similar to those of the many mechanical processes involving fuels, such as the fuel injection stage in internal combustion engines. For instance, for Syngas and NG, the fuel injection process is generally performed at a temperature and an absolute pressure of around 600 K [30,31] and 1atm [31], respectively, so that the fuels, throughout this step, are at chemical equilibrium (i.e., there are no combustion reactions).

Thus, calculations based on quantum mechanics and statistical thermodynamics were performed in order to obtain the following quantities for Syngas and the NG/Syngas mixtures: internal energy (U), enthalpy (H), Gibbs free energy (G) and entropy (S). These quantities were calculated for temperatures from 0.5 K to 1500 K. To obtain these thermodynamic quantities for the fuels, we first modeled each one of their major components. This modeling was, initially, given by a conformational search [32] of the molecules, where the first energy minimization for the molecular structures was performed using the classical method of Molecular Mechanics (MM+) [33,34] through Hyperchem 7.5 software [35]. During these calculations, torsion and bond angles, along with lengths of atomic bonds, were randomly disturbed in order to verify, based on the classical model, the molecular conformation with lower energy for each major component of each fuel.

After the conformational searches, a second energy minimization process was performed for each molecule, now utilizing Gaussian 09 W software [36] for simulations based on the DFT model [27,28]. In these simulations we used the B3LYP functional [37,38], along with the sophisticated basis set: 6–311++g(d,p) [39], which is recommended for NG thermodynamic DFT analysis [40]. Geometry optimization provided the molecular conformations with lower energy for each component of both Syngas and NG fuels.

The third stage of simulations consisted of frequency calculations (IR and Raman) [41,42] of the chemical species, where the same functional and basis set considered previously in the geometry optimization was used. From this calculation the thermodynamic properties presented in this study were obtained. No imaginary frequencies were observed for the molecular structures, which mean that the geometries were well optimized. Thus, for these calculations, each molecular system was simulated through the canonical ensemble [29], where partition functions were obtained for the following motions: translational, rotational, vibrational and electronic, and the monomolecular polyatomic gas models ware considered. These functions are given by:

$$q_t = \left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}} V(\text{translational motion}), \tag{1}$$

where m, k_B, h end V are, respectively, the mass particle, Boltzmann and Planck constants, and the molecular volume.

$$q_r = \frac{1}{\sigma_r}\left(\frac{8\pi^2 I k_B T}{h^2}\right)(\text{rotational motion}), \tag{2}$$

I being the moment of inertia of the molecular structures, and σ_r corresponding to their symmetry number.

$$q_\upsilon = \prod_k \frac{e^{-\frac{\Theta_{v,k}}{2T}}}{1 - e^{-\frac{\Theta_{v,k}}{T}}}(\text{vibrational motion}), \tag{3}$$

with $\Theta_{v,k} = h\nu_k/k_B$, with ν being the vibrational frequency associated with the k-th normal mode of vibration.

$$q_e = \omega_0 e^{-\frac{\varepsilon_0}{k_B T}} + \omega_1 e^{-\frac{\varepsilon_1}{k_B T}} + \omega_2 e^{-\frac{\varepsilon_2}{k_B T}} + \ldots(\text{electronic contribution}), \tag{4}$$

where ω is the degeneracy of energy levels and ε_n corresponds to the energy of the n-th level. Thus, once the energy of the first excited state is much greater than k_BT, all excited states are inaccessible, regardless of temperature. However, the internal energy and entropy of the system are obtained, respectively, from Eq. (5) and (6):

$$U = N k_B T^2 \left[\frac{\partial \ln(q_t q_r q_\upsilon q_e)}{\partial T}\right]_V, \tag{5}$$

$$S = R\ln(q_t q_r q_\upsilon q_e) + RT\left[\frac{\partial \ln(q_t q_r q_\upsilon q_e)}{\partial T}\right]_V; \tag{6}$$

where N is the number of molecules and R corresponds to the universal gas constant.

In order to obtain the thermodynamic properties of Syngas and NG from the properties of their components, we calculated the quantities of each of the chemical species in the fuel compositions, such that the properties of mixtures were obtained from weighted averages, where we take into account that both fuels (Syngas and