

THERMODYNAMIC CONSIDERATIONS OF THE CO_x HYDROGENATION REACTION TO LIGHT OLEFINS USING CARBON-NEUTRAL FEEDSTOCK MIXTURES

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ABSTRACT

Light olefins are considered the backbone of chemical industry, and a broad variety of derivatives, used in our daily lives, are produced from these building blocks. Notably, it is estimated that the C₂₋₄ demand will face an annual growth of 3.5% by 2030, as a combined result of global population growth and rising living standards. The current leading technology for light olefins production is the steam cracking of natural gas and/or crude oil fractions but this process is linked with a high carbon footprint. Concerns associated with the depletion of fossil fuels and the threat of global warming have recently initiated efforts to explore alternative pathways and feedstocks to produce light olefins through CO_x hydrogenation by employing either excess RES-powered electrolytic hydrogen combined with captured CO₂ industrial emissions or syngas mixtures generated through biomass gasification or biofuels reforming. Therefore, the present work aims to examine the thermodynamic aspects of the CO_x hydrogenation to light olefins at a range of temperatures and pressures of industrial practice by feeding several carbon-neutral CO_x-H₂ mixtures. For this end, the Aspen Plus software and the Gibbs free energy minimization method have been compiled in a series of simulation scenarios.

Keywords: Thermodynamic analysis, CO_x hydrogenation, Light olefins production, Industrial CO₂ capture, Bio-syngas

INTRODUCTION

Light olefins, C₂₋₄, are the top chemicals in terms of global production rates with an annual ethylene and propylene capacity of ca. 150 million tons [1], and are deemed as the key building blocks for a range of products, such as plastics, gels, fibers, pharmaceuticals, cosmetics, etc. Olefins are industrially produced by the steam cracking of naphtha or the thermal ethane cracking, both highly energy intensive processes that charge each ton of olefin with 0.75 up to 11.5 tons of CO₂ emissions, depending on the employed production route, raw materials and energy sources (usually 2 – 5 t_nCO₂/t_nC₂₋₄ for oil and natural gas) [2]. EU Green Deal recognizes the necessity to detach chemical industries from fossil carbon towards the transition to complete decarbonisation at 2050. Recently, new approaches to generate light olefins by neutral carbon sources and renewables have been proposed including among others the employment of syngas by biofuels reforming and biomass gasification, as well as, the hydrogenation of industrially captured CO₂ emissions by renewable electrolytic hydrogen.

CO₂ to C₂₋₄ olefins is a catalysis benchmark and includes a complicated reaction system due to i) the multiple reaction pathways of CO₂ hydrogenation to various products (CO, CH₄, light olefins, higher hydrocarbons, methanol, etc.) and ii) its sensitivity to operational conditions (e.g., temperature, pressure, H₂/CO₂/CO feed ratio, presence of other substances) and catalyst properties (e.g., active phases, dispersion, acidity-basicity). The challenges of this process highlight the importance of obtaining a thorough understanding of the reaction's thermodynamics prior to catalytic studies. To the best of the authors knowledge, there are only a few relevant works in literature thermodynamically exploring the effect of operational temperature, pressure and feed composition on conversion, selectivity and light olefins/paraffins product distribution [3], [4].

In the present study, an extensive thermodynamic analysis of industrially relevant CO_x hydrogenation reaction systems to light olefins is conducted, using the Aspen Plus software and the Gibbs free energy minimization method. More specifically, carbon-free and renewable H₂/CO_x upstream industrial feed mixtures were considered and the performance in terms of conversion, selectivity and yields to light olefins was explored over a wide range of operational parameters

(i.e., temperature, pressure, H₂/CO_x reactants ratio). Moreover, the methodology took into consideration the presence of other chemical substances (CH₄, H₂O) existing in practical feedstock mixtures.

METHODOLOGY

For the current thermodynamic analysis, the ASPEN Plus software was used to calculate the equilibrium compositions, utilizing the Gibbs reactor (R_{Gibbs}). The non-ideal behavior in Gibbs energy values was introduced by the Soave-Redlich-Kwong thermodynamic package in order to calculate the substantial properties per component and per reaction mixture. Ethylene, propylene, butylene, hydrogen and carbon dioxide were considered as the only products of the aforementioned reaction system. It is highlighted that paraffins were excluded from the study since the aim was to identify the pathway towards olefins (in other words, paraffin production is thermodynamically favoured and masks the production of olefins through a tailor-made catalytic system). The equations that define the conversion of CO₂, the selectivity and yields of light olefins (C_nH_m) are presented as follows:

$$X_{CO_2}(\%) = \frac{CO_{2 \text{ inlet}} - CO_{2 \text{ outlet}}}{CO_{2 \text{ inlet}}} \times 100 \quad (1)$$

$$S_{C_nH_m}(\%) = \frac{nC_nH_m \text{ outlet}}{\sum_1^n nC_nH_m \text{ outlet}} \times 100 \quad (2)$$

$$Y_{C_nH_m}(\%) = \frac{X_{CO_2} \times S_{C_nH_m}}{100} \quad (3)$$

RESULTS AND DISCUSSION

For the thermodynamic calculations a reacting mixture consisting of captured CO₂ and electrolytic hydrogen by excess RES power is initially considered. Figure 1 depicts the effect of operational temperature on the CO₂ conversion and light olefins selectivity at various pressures ranging from 10 to 30 bar and for a stoichiometric H₂/CO₂ = 3. The increase of the temperature leads to lower CO₂ conversions for all employed pressures, as expected due to the exothermic nature of the investigated reactions. Butylene is the main olefin product at low temperatures following a decreasing trend with temperature. On the other hand, ethylene starts to formulate at ca. 300 °C and increases with temperature and appears to be the prevailing olefin at higher temperatures. The corresponding selectivity profile for propylene follows a volcano behavior showing a maximum at approximately 500 °C. In general, higher pressures favour butylene selectivity, whereas ethylene/propylene selectivities decrease with pressure.

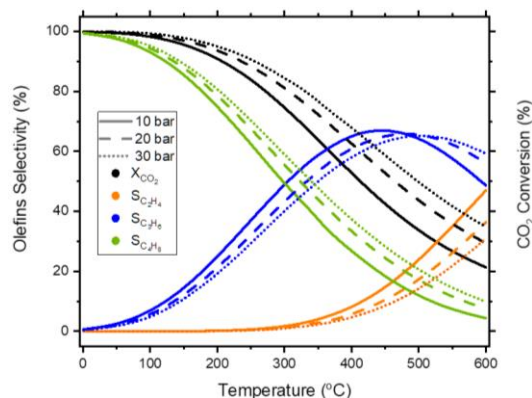


Figure 1: Effect of temperature on C₂₋₄ selectivity and conversion at 10, 20 and 30 bar for a stoichiometric H₂:CO₂ feed

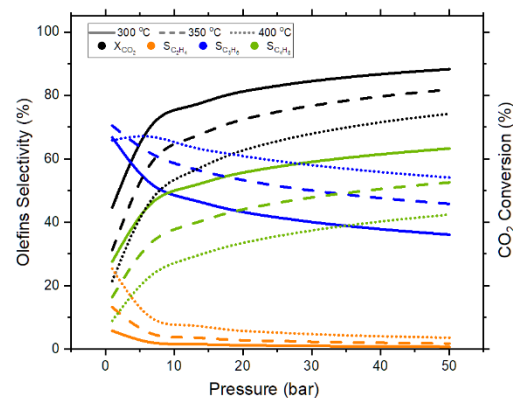


Figure 2: Effect of pressure on C₂₋₄ selectivity and conversion at 300, 350 and 400 °C for a stoichiometric H₂:CO₂ feed

As a volume-reducing reaction system, the conversion of CO₂ is expected to increase with pressure according to the Le Chatelier's principle. This is confirmed in Figure 2, which presents the effect of pressure (1 – 50 bar) at three different temperatures (300, 350 and 400 °C) and at stoichiometric feed ratio H₂/CO₂ = 3. The selectivities for ethylene and propylene decrease with pressure, whereas butylene exhibits an increasing trend with the operating pressure being the main product for pressures higher than 10 bar and T= 300 °C. At 400 °C, propylene exhibits the highest selectivity in the whole pressure range. At 350 °C, propylene's selectivity is higher than butylene's for pressures up to 30 bar, while above 30 bar an inverse behavior is observed. Figure 3 shows the effect of H₂:CO₂ molar feed composition from sub- to over-stoichiometric ratios (1 – 9) at three different temperatures (300, 350 and 400°C) and for the pressures of 20 and 30 bar. It is clearly observed that the CO₂ conversion linearly increases with the feed ratio increase, while the corresponding effect on olefins selectivity is essentially negligible. Finally, in the case of upstream derived syngas mixtures from biomass gasification or biofuel reforming containing CO₂, CO, H₂, CH₄ and H₂O, the results revealed that CO₂-rich syngas mixtures favor the selectivities of ethylene and propylene, while the corresponding values for butylene are suppressed.

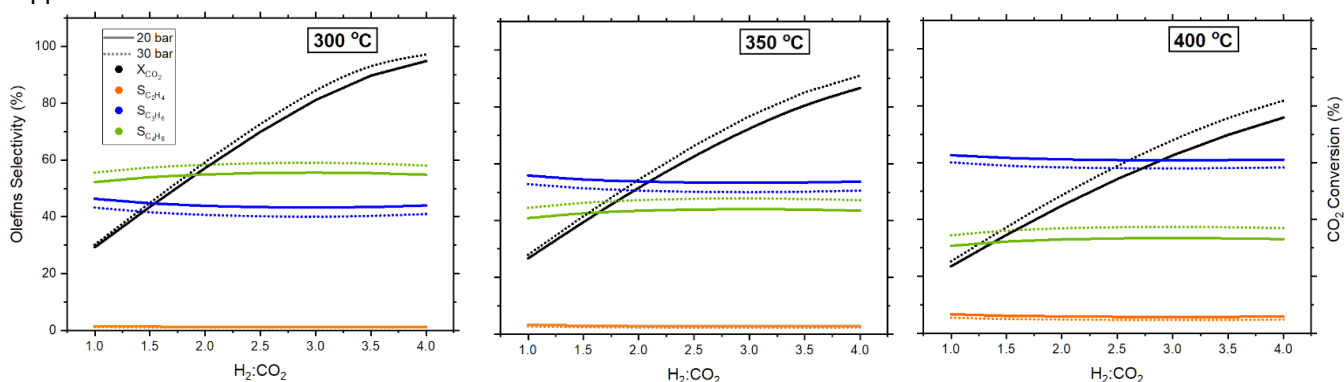


Figure 3: Effect of H₂:CO₂ feed molar ratio on C₂₋₄= selectivity and CO₂ conversion at 300, 400 and 500 °C and for 20 and 30 bar pressures

CONCLUSIONS

A detailed thermodynamic analysis of CO_x hydrogenation to light olefins was conducted and the effect of the operation temperature, pressure and feed composition on the conversion and selectivity to light olefins was thoroughly investigated. As an exothermic and mol-reducing reaction, the conversion is favored at low temperatures and high pressures, while the increase in H₂ feed concentration shift the reaction equilibrium to the right. In the case of syngas mixtures derived by upstream biomass gasification or biofuel reforming processes with high CO₂ contents, the selectivities to ethylene and propylene are enhanced at the expense of butylene formation.

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