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Simulation of vegetable oils steam reforming process and comparison with literature experimental data

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***Abstract*—**The steam reforming process for vegetable oils has been simulated in ChemCad 6.4 simualtion package around atmospheric pressure, 500 to 700°C and with steam-to-carbon (S/C) ratios of 3, 6 and 9. The simulation results were compared to experimental data reported in literature in terms of feed carbon conversion to gas product and gas product composition. Simulated data satisfactorily agree with experimental and both show that the major components in the reforming gas product are H_2, CO_2, CO and CH_4.

***Key words*—**Simulation, Steam reforming, vegetable oil

I. Introduction

VEGETABLE oils form of one group of renewable energy sources that have drawn research focus around the globe. Vegetable oils are subjected to varied treatment processes in order to produce biofuel. One of the most reported process is *trans*-esterification of vegetable oils for biodiesel production. While research is still on-going to improve the economics for vegetable oils *trans*-esterication process, other processes such as vegetable oils cracking [1,2], steam reforming [3,4] and hydrotreatment [5-7] have also received lot of research interest. Marquevich *et al.* [3,4] have shown that sunflower oil could be satisfactorily converted into H_2 by steam reforming using commercial based catalysts. They have also indicated that equivalent yields and rates of H_2 formation can also be obtained with other vegetable oils such as rapeseed oil, corn oil, and soybean used as feedstocks for the process [4]. Most of these studies report kinetic data that are usually acquired from experimental setup requiring high temperatures. Very little is reported on equilibrium conversions of vegetable oils and product compositions during these processes. This information is useful for process design purposes. This study aims at developing a simulation model for vegetable oils steam reforming using ChemCad 6.4 simulation package and validating the modeled data by comparison with reported experimental data in the literature.

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II. Methodology

The simulation of steam reforming for vegetable oils was performed with ChemCad 6.4 simulation package. The feed to the reforming reactor was chosen as 1 000 Kg/h of vegetable oil and mixed with steam to achieve S/C ratios of 3, 6 and 9. The simulation was performed at 1 bar between 500 and 700°C. The vegetable oil was modeled by triolein and the reforming process was modeled by Gibbs free energy minimization in ChemCad. The Gibbs reactor model is based on the principal that at chemical equilibrium the total Gibbs energy of the system has its minimum value. By attempting to minimize the total energy of the system, individual equilibrium constants are not considered. Rather, the possible reaction species are noted, and the distribution of these species is established using a general mathematical technique to give a minimum free energy for the system [8]. The selected possible components in the predicted equilibrium product included H_2, CO, CO_2, alkanes (C_1 to C_{15}), olefins (C_2 to C_{15}), cyclic hydrocarbons, aromatic compounds, light ketones, alcohols, carboxylic acids and carbon. All the selected components with their physical and chemical properties were available in ChemCad 6.4 components database. The simulated results were compared with experimental data from the literature for validation.

III. Results And Discussion

To validate the process model, the modeled data were compared with experimental data reported in literature. Marquevich *et al.* [4] presented experimental results for the steam reforming of sunflower oil with nickel-based commercial (ICI 46-1, ICI 46-4 and UCI G90C) and research (UdeS and HT) catalysts. They used an isothermal fixed-bed tubular reactor with S/C ratios of 3, 6, 9 and temperatures between 500 and 630 °C. They used low reactor pressures and most of their experiments were conducted between 1 and 1.7 bar with only a very limited number of experiments performed below 1 bar and above 2.11 bar. For this pressure range used, their data don't indicate any significant effect of pressure on the experiments results. Therefore, these data were found suitable for comparison with the modeled data in this study. The major products of the modeled vegetable oils steam reforming are H_2, CO_2, CO, CH_4 and C, consistent with the reported experimental data with the only

difference that Marquevich *et al.* [4] did not indicate whether they observed carbon formation or not. Experimental and modeled data were compared in terms of feed carbon conversion to gas (CO, CO_2 and CH_4) and reforming gas product composition. To facilitate comparison, the experimental data reported by Marquevich *et al.* [4] for the steam reforming of sunflower oil were plotted on the same graph with our modeled data. Figure 1 shows the modeled and experimental feed carbon conversion to gas product. For S/C ratio of 9 (Fig 1c), all experimental feed carbon conversions at various temperatures are below the modeled conversions. This makes sense as our data were modeled by the system's Gibbs energy minimization which predicts equilibrium conversions that cannot be thermodynamically overcome by experiments. The same observation is evident for the data with S/C of 6 (Fig. 1b) with one of the experimental data with catalyst HT almost matching the predicted equilibrium feed carbon conversion at 600°C. The data for S/C of 3 show two experimental points above the predicted equilibrium conversions (Fig. 1a) but most of the plotted experimental points are well below the modeled data. Allowing for some possible minor errors, our modeled carbon conversions agree well with the experimental data in terms of thermodynamic conversion limitations. Also, the modeled data, in agreement with the experimental data, show an increase in feed carbon conversion to gas product with an increase in temperature. Fig. 2 shows H_2 mol.% in the reforming gas product. Our model predicts H_2 contents of 72-76% in the reforming gas products compared to experimental values around 70%. These data agree well with the experimental data and both show a slight decrease in H_2 mol.% in the gas product with an increase in temperature and are not significantly affected by S/C ratios. The CO_2 mol.% in the gas product are summarized in Fig. 3. For the data with S/C ratio of 3, experimental CO_2% where between 20 and 27% compared to 16 and 18% predicted for equilibrium conditions. Experimental and predicted data get even closer for S/C ratios of 6 and 9 where they all vary between 20 and 27% with a single outlier for the UdeS catalyst at 496°C. These data also show that predicted and experimental CO_2 mol.% in the reforming gas product are well comparable.

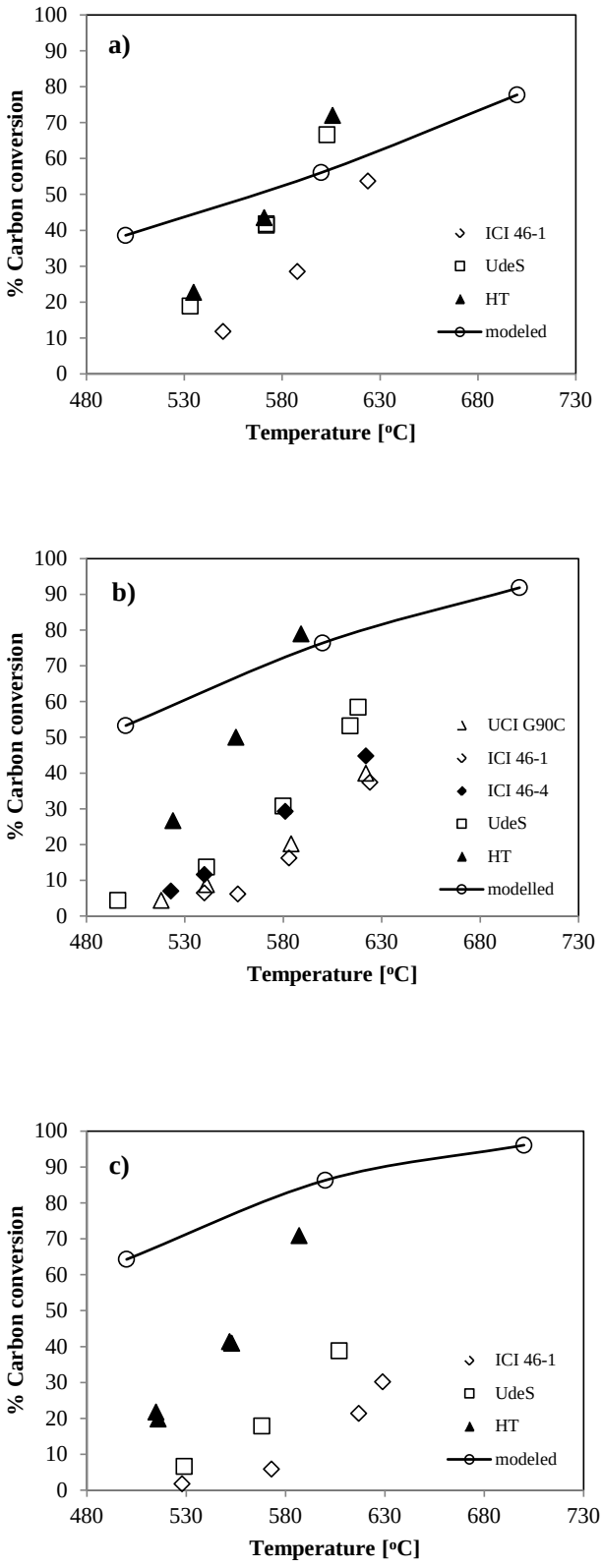
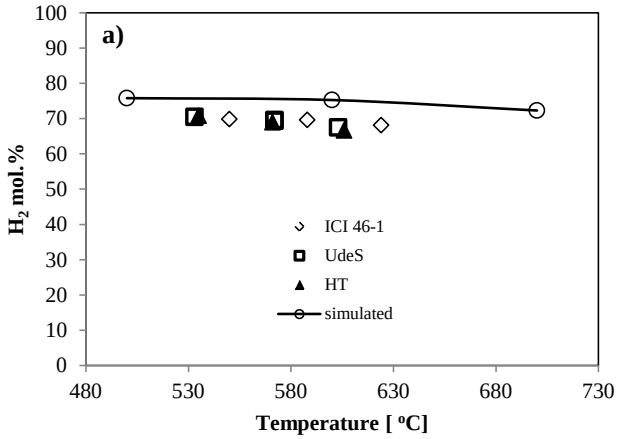
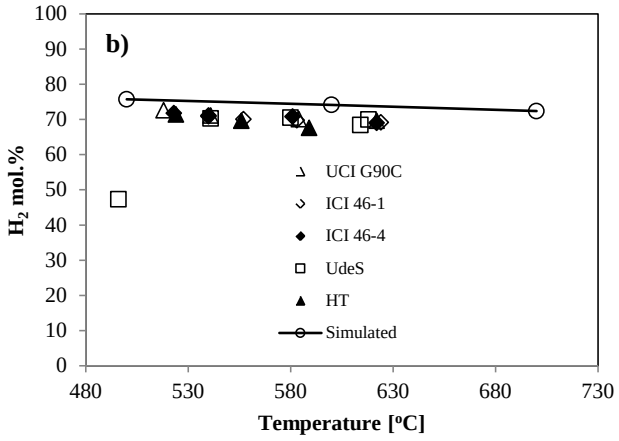


Fig.1. Modeled and experimental (redrawn from ref. [4]) feed carbon conversions to gas product as a function of reforming temperature and S/C ratios: a) S/C ratio = 3; b) S/C ratio = 6; c) S/C ratio = 9





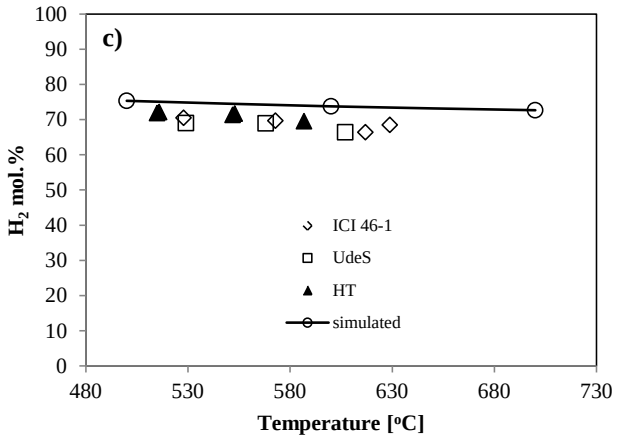
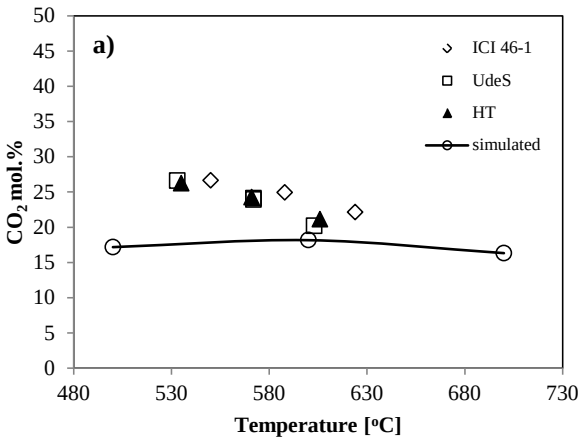
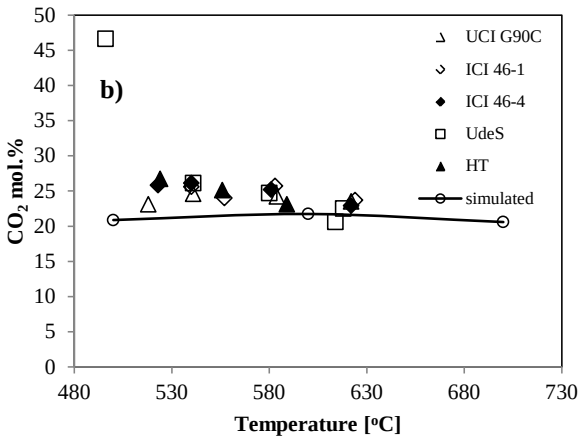


Fig. 2 Modeled and experimental (redrawn from ref. [4]) H_2 mol.% in the reforming gas product as a function of reforming temperature and S/C ratios: a) S/C ratio = 3; b) S/C ratio = 6; c) S/C ratio = 9





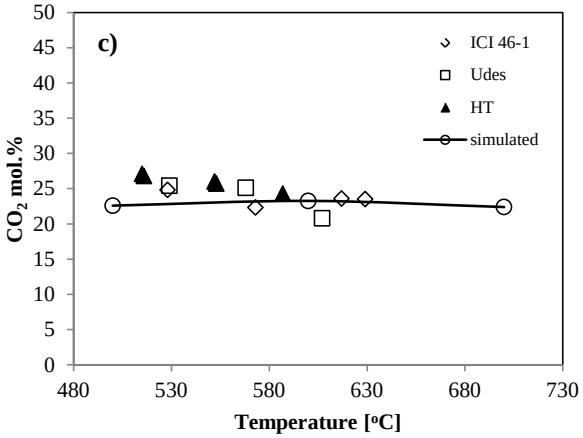


Fig. 3 Modeled and experimental (redrawn from ref. [4]) CO_2 mol.% in the reforming gas product as a function of reforming temperature and S/C ratios: a) S/C ratio = 3; b) S/C ratio = 6; c) S/C ratio = 9

CO and CH_4 mol.% in the gas product are presented in Fig. 4 and Fig. 5 respectively. These simulated data also agree with the experimental are they are the same order of magnitude.

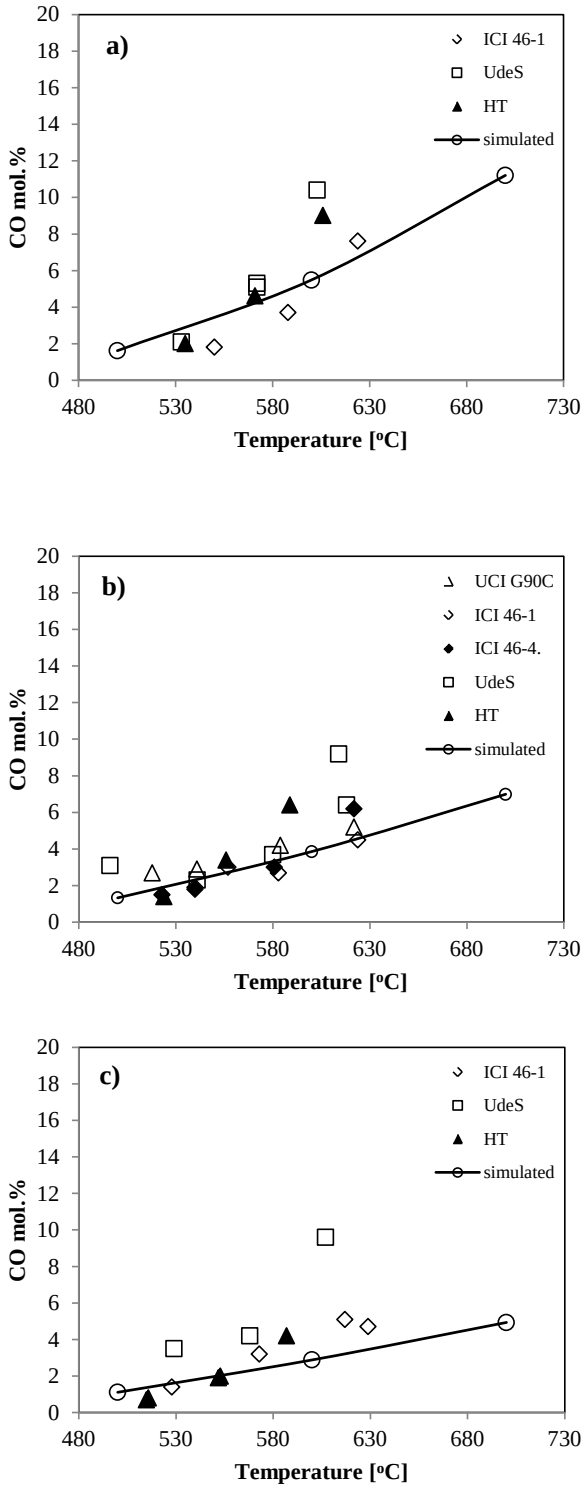


Fig. 4 Modeled and experimental (redrawn from ref. [4]) CO mol.% in the reforming gas product as a function of reforming temperature and S/C ratios: a) S/C ratio = 3; b) S/C ratio = 6; c) S/C ratio = 9

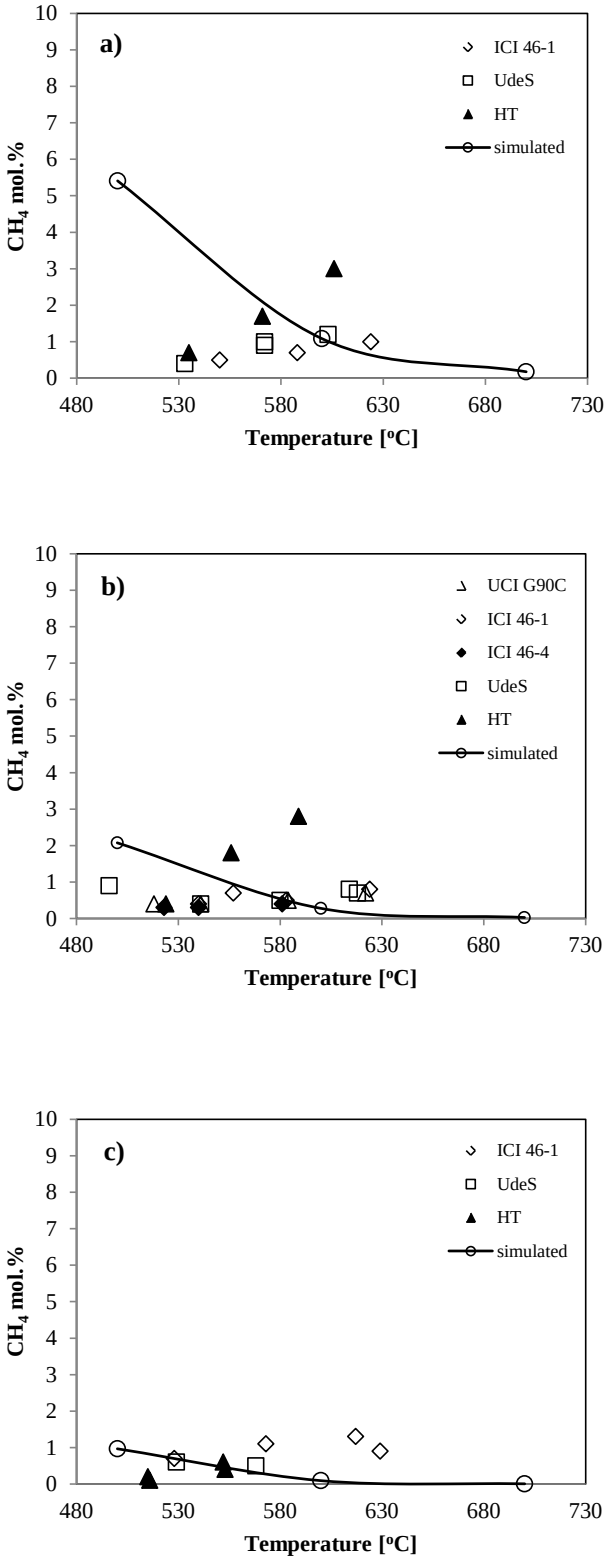


Fig. 5 Modeled and experimental (redrawn from ref. [4]) CH_4 mol.% in the reforming gas product as a function of reforming temperature and S/C ratios: a) S/C ratio = 3; b) S/C ratio = 6; c) S/C ratio = 9

IV. Conclusion

Vegetable oils steam reforming was modeled with ChemCad 6.4 simulation package where vegetable oils were represented by triolein. The simulated data were compared with literature experimental data for sunflower oil steam reforming in terms of feed carbon conversion to reforming gas product and gas product composition as function of temperature. Our modeled carbon conversions agree well with literature experimental data in terms of thermodynamic conversion limitations and variations with reaction temperatures. The major components formed in the reforming gas products were H_2, CO, CO_2 and CH_4 as also reported by experiments. Our model predicts comparable H_2 contents (72-76% in the reforming gas products) to literature experimental values around 70% in the 500-630^oC temperature range. The data for simulated CO_2, CO and CH_4 mol.% in the reforming gas product also agree with the reported experimental data. The present study has shown that simulation of the vegetable oils steam reforming using ChemCad 6.4 simulation package with Gibbs free energy minimization model leads to satisfactory results that are comparable to literature experimental data.

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