Steam Reforming of Vegetable Oils: Equilibrium Product Selectivity

K. Jalama

Abstract— **Vegetable oils are triglyceride-based biomass that can be processed in various ways to produce biofuel. Steam reforming of these oils can be used to produce hydrogen, synthesis gas or gaseous fuel. In the present study, ChemCad 6.4 simulation package was used to predict equilibrium product composition for a modeled vegetable oil steam reforming as a function of temperature (400-1000^{o}C) and steam amounts added to the feed (10 to 90 wt.%). The obtained data predict that for maximum H_2 production from vegetable oil through steam reforming, high steam content in the feed is required and that steam contents of ca. 50 wt.% in the feed are optimal for the production of synthesis gas suitable for the Fischer-Tropsch process (H_2/CO ratio of 2/1) over a temperature range of 600^{o}C to 1000^{o}C.**

Index Terms— **Equilibrium products, steam reforming, vegetable oils**

I. INTRODUCTION

RENEWABLE energy sources significantly receive more attention than ever before. This is mainly due to the increase in energy demand across the world while fossil energy sources are dwindling and to the increase in environmental challenges. Vegetable oils are triglyceride-based biomass which can be transformed into biofuel through various processes such as trans-esterification with an alcohol to biodiesel, cracking and reforming to produce gas and liquid biofuel. Biofuels are considered to be ‘‘*CO_2 neutral*’’ as they do not add to the CO_2 levels in the atmosphere since they are from plant sources which typically remove CO_2 from the atmosphere, and release the same amount when burnt [1]. Steam reforming of vegetable oils is a process of adding heat to the oil in presence of steam and a suitable catalyst. Marquevich *et al.* [2] have reported H_2 production by catalytic reforming of vegetable oils. Gornay *et al.* [3] showed that atmospheric pressure thermal cracking of waste cooking oil in the presence of steam (steam reforming) would be a potential option, particularly when the operating conditions direct the process in order to produce specific target bioenergy vectors: hydrogen, synthesis gas, or gaseous fuel.

Most studies only report kinetics of steam reforming and the information on thermodynamic equilibrium product is very limited. This information is very important for further process development and improvement. The present study aims at predicting the equilibrium product selectivity for vegetable oil steam reforming and determining the operating conditions that favor the production of H_2 and synthesis gas suitable for the Fischer-Tropsch process.

II. METHODOLOGY

ChemCad 6.4 simulation package was used to predict equilibrium product composition for a modeled vegetable oil steam reforming as a function of temperature and amounts of steam added to the feed (10 to 90 wt.%). A temperature range of 400-1000^{o}C and steam contents of 10, 30, 50, 70 and 90 wt.% in the feed were considered. A process pressure of 1 bar was used throughout this study. The vegetable oil was modeled by triolein and the steam 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 equilibria 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 [4]. 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 acid and solid carbon. Except for the solid carbon, all the selected components with their physical and chemical properties were available in ChemCad components database. The solid carbon was added to the ChemCad components database and was modeled as graphite. The graphite heat capacity polynomial coefficients determined by Butland and Maddison [5] were used for the simulation. The enthalpy and Gibbs energy of formation for the solid carbon were entered as 0 kJ/mol.

III. RESULTS AND DISCUSSION

An example of equilibrium products distribution as a function of temperature for a feed containing 10 wt.% steam is presented in table 1. The major reaction products were H_2, CO, CO_2, light hydrocarbons and aromatics in agreement with earlier experimental catalytic reforming studies [3, 6, 7]. H_2 is a valuable fuel as it can be used in fuel cells for power generation. The mixture of H_2/CO, referred to as synthesis gas, is a useful feedstock for liquid fuel production using the Fischer-Tropsch (FT) process. For the FT process, an H_2/CO ratio around 2/1 is recommended.

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TABLE I

PREDICTED EQUILIBRIUM PRODUCTS AS A FUNCTION OF TEMPERATURE FOR A FEED CONTAINING 10 WT.% STEAM

Products		**Product molar composition (%, dry basis)**						
Components	**Chemical formula**	**400°C**	**500°C**	**600°C**	**700°C**	**800°C**	**900°C**	**1000°C**
Hydrogen	(H_2)	0.2907	1.2677	3.9543	9.3617	17.8981	28.3830	38.6164
Carbon monoxide	(CO)	16.3781	27.8559	29.2428	28.6869	27.5647	26.1617	24.7872
Carbon dioxide	(CO_2)	8.1943	1.1862	0.1253	0.0192	0.0038	0.0009	0.0003
Water	(H_2O)							
Triolein	($C_{57}H_{104}O_6$)							
Methyl oleate	($C_{19}H_{36}O_2$)							
Ethyl oleate	($C_{20}H_{36}O_2$)							
Coke	C							
Paraffins		**62.7489**	**59.5072**	**56.6334**	**51.5013**	**43.4236**	**33.4734**	**23.7240**
Methane	(CH_4)	62.7161	59.4725	56.5970	51.4655	43.3923	33.4495	23.7077
Ethane	(C_2H_6)	0.0327	0.0347	0.0363	0.0357	0.0312	0.0239	0.0163
N-propane	(C_3H_8)	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	
N-butane	(C_4H_{10})							
N-pentane	(C_5H_{12})							
N-hexane	(C_6H_{14})							
N-heptane	(C_7H_{16})							
N-octane	(C_8H_{18})							
N-nonane	(C_9H_{20})							
N-decane	($C_{10}H_{22}$)							
N-Undecane	($C_{11}H_{24}$)							
N-dodecane	($C_{12}H_{26}$)							
N-tridecane	($C_{13}H_{28}$)							
N-tetradecane	($C_{14}H_{30}$)							
N-pentadecane	($C_{15}H_{32}$)							
Olefins		**0.0011**	**0.0072**	**0.0310**	**0.0959**	**0.2279**	**0.4335**	**0.6871**
Ethylene	(C_2H_4)	0.0011	0.0069	0.0301	0.0937	0.2236	0.4268	0.6781
Propylene	(C_3H_6)	0.0001	0.0003	0.0009	0.0021	0.0040	0.0061	0.0077
1-butene	(C_4H_8)							
1,3-butadiene	(C_4H_6)				0.0001	0.0002	0.0006	0.0012
1-pentene	(C_5H_{10})							
1-hexene	(C_6H_{12})							
1-heptene	(C_7H_{14})							
1-octene	(C_8H_{16})							
1-nonene	(C_9H_{18})							
1-decene	($C_{10}H_{20}$)							
1-undecene	($C_{11}H_{22}$)							
1-dodecene	($C_{12}H_{24}$)							
1-tridecene	($C_{13}H_{26}$)							
1-tetradecene	($C_{14}H_{28}$)							
1-pentadecene	($C_{15}H_{30}$)							
Cyclic hydrocarbons								
Cyclopentene	(C_5H_8)							
Cyclopentane	(C_5H_{10})							
Cyclohexene	(C_6H_{10})							
Cyclohexane	(C_6H_{12})							
Cycloheptene	(C_7H_{12})							
Cycloheptane	(C_7H_{14})							
Aromatics		**12.3869**	**10.1757**	**10.0131**	**10.3351**	**10.8820**	**11.5474**	**12.1851**
Benzene	(C_6H_6)	11.1004	9.4611	9.4912	9.9102	10.5242	11.2427	11.9281
Toluene	(C_7H_8)	1.2302	0.6925	0.5094	0.4165	0.3519	0.3005	0.2540
Ethylbenzene	(C_8H_{10})	0.0042	0.0021	0.0015	0.0012	0.0010	0.0008	0.0006
O-xylene	(C_8H_{10})	0.0130	0.0052	0.0030	0.0020	0.0014	0.0010	0.0007
M-xylene	(C_8H_{10})	0.0280	0.0105	0.0057	0.0037	0.0025	0.0017	0.0011
P-xylene	(C_8H_{10})	0.0112	0.0043	0.0023	0.0015	0.0010	0.0007	0.0005
Short chains alcohols, ketone and carboxylic acids								
Methanol	(CH_4O)							
Ethanol	(C_2H_6O)							
Propanol	(C_3H_8O)							
Acetone	(C_3H_6O)							
Acetic acid	($C_2H_4O_2$)							
Acrylic acid	($C_3H_4O_2$)							
Total		**100**	**100**	**100**	**100**	**100**	**100**	**100**

Light hydrocarbons and aromatics can be used as fuel. CO_2 is an undesired product as it is a loss of carbon and decreases the process carbon efficiency. The system overall enthalpy minimization did not predict any solid carbon deposition which was observed in some experimental catalytic studies (3, 6, 7). This could suggest that solid carbon is an intermediate product but not an equilibrium product for vegetable oil steam reforming.

Fig. 1 shows the calculated H_2 molar percentage in the reforming product as a function of temperature and the amount of steam added to the oil feed.

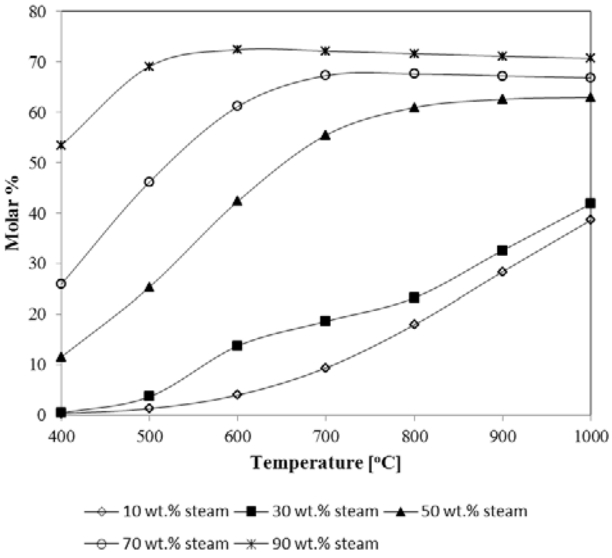

Fig. 1. Molar contents (dry basis) of H_2 in the predicted reforming product as function of temperature and amounts of steam added to the oil feed

The data show that H_2 production increases with the increase of the steam amounts added to the feed. For example at 400°C, almost no H_2 is produced for the feed containing up to 30 % steam. The produced H_2 molar composition in the product increases with the temperature and reaches 39 and 42% at 1000°C for the feed containing 10 and 30% steam respectively. As the amount of steam in the feed is increased to 50 %, an H_2 composition of ca. 10% is predicted at 400°C and increases with the reaction temperature up to ca. 800°C where it almost flattens at 62-63%. Further increase of steam in the feed shows a maximum in H_2 production at ca. 800°C (ca. 67%) and 600°C (ca. 72%) for the feed containing 70 and 90% respectively. These data suggest that for maximum H_2 production from vegetable oil through steam reforming, high steam contents in the feed are required. In terms of process, this creates a penalty for high energy requirements for the feed but also an advantage of operating at lower temperatures. A proper process energy requirements analysis (not covered in this study) would determine whether the lower operating temperature will offset the high energy requirements for the feed.

Fig. 2 shows the carbon atom based selectivity to CO, CO_2, CH_4 and aromatics as a function of reforming temperature and steam contents of the feed. For the feed with 10% steam, the aromatics have the highest selectivity which passes through a minimum at ca. 500°C and further increases with the reaction temperature (Fig. 2a). This selectivity drops to ca. 0% from 500°C for the feed containing 30% steam (Fig. 2b) and for the whole temperature range, i.e. 400 – 1000°C for the feed containing 50, 70 and 90% steam. This can be explained by an increase in steam-derived H_2 in the reactor for the feed with high steam contents. The CH_4 selectivity decreases with the increase in temperature for the feed containing 10 to 90% steam (Fig. 2 a-e) and reaches zero, i.e. the CH_4 becomes an intermediate product from ca. 600 and 800°C for the feed containing 90 and 70% steam respectively (Fig. 2 d and e). This suggests that the produced CH_4 possibly undergoes steam reforming to CO and H_2 as the temperature and the steam contents in the feed increase. The operating conditions leading to the CH_4 complete disappearance from the equilibrium product spectrum are the same as those for the maximum H_2 production (Fig. 1) and hence support the above explanation. The CO selectivity increases with the increase in steam contents (for 10, 30 and 50% steam) and temperature up to a point when it flattens off (Fig. 2 a-c). With higher steam contents (70 and 90% steam), the CO selectivity increases with temperature but decreases with steam contents that favor more CO_2 formation. This indicates that more carbon is lost at higher steam contents possibly via the water gas shift reaction. To select optimal conditions for synthesis gas production, the H_2/CO ratio as function of steam contents in the feed and reaction temperature (Fig. 3) must be considered. The data in Fig. 3 suggest that for the production of synthesis gas as a feed to an FT process, steam contents in excess of 50% must be avoided as they will lead to an H_2/CO ratio well above 2/1. Steam contents of ca. 50% in the feed are optimal for FT syngas production as they lead to H_2/CO ratios of ca. 2/1 over a wide range of temperature (600°C to 1000°C).

IV. CONCLUSION

This study aimed at predicting the equilibrium product selectivity for vegetable oil steam reforming and determining favorable operating conditions for the production of H_2 and synthesis gas suitable for the Fischer-Tropsch process. The obtained data predict that for maximum H_2 production from vegetable oil through steam reforming, high steam contents in the feed are required and that steam contents of ca. 50 wt.% in the feed are optimal for the production of synthesis gas suitable for the Fischer-Tropsch process (H_2/CO ratio of 2/1) over a temperature range of 600°C to 1000°C.

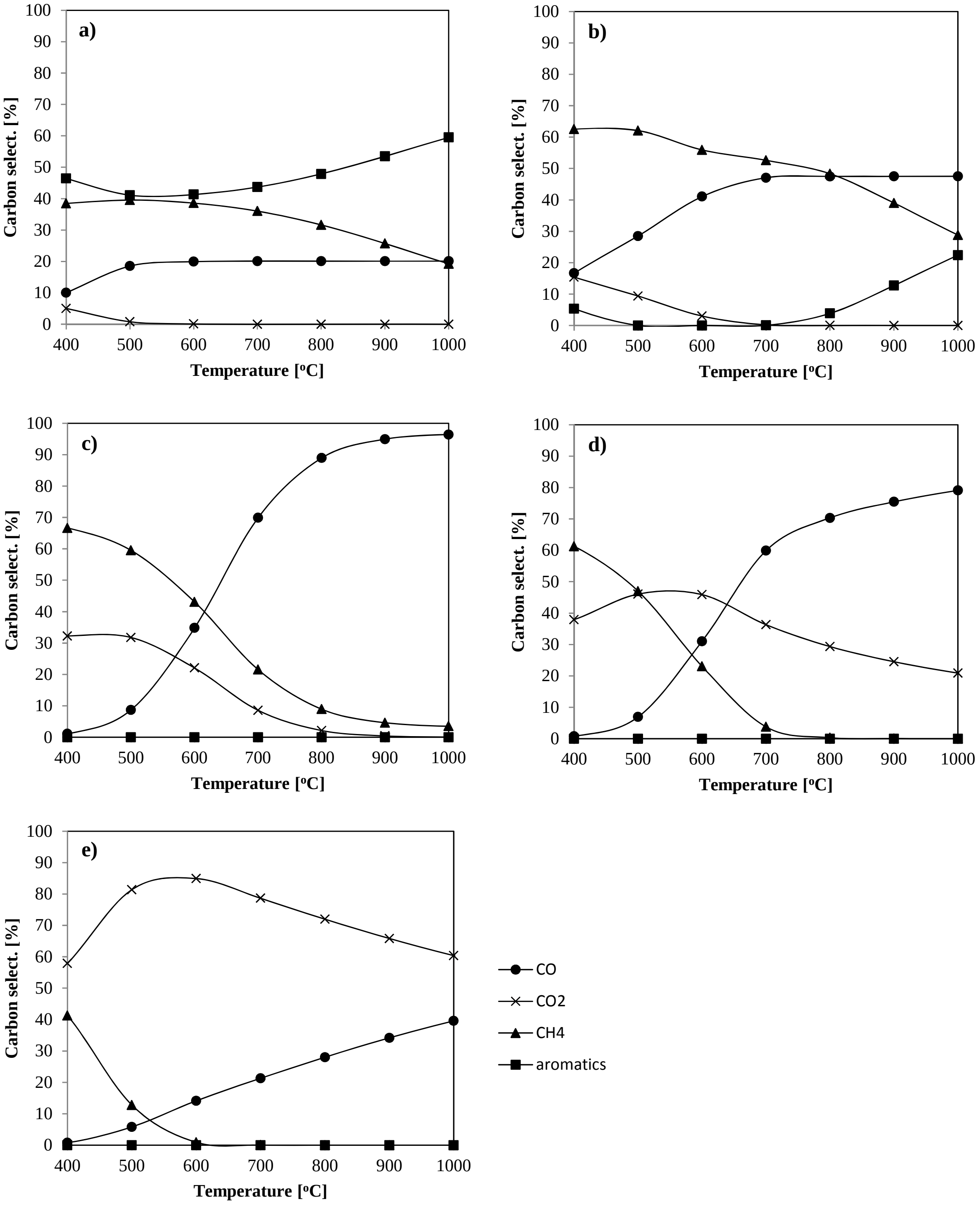

Fig. 2. Effect of steam contents in the feed and reforming temperatures on the carbon-based selectivity to CO, CO_2, CH_4 and aromatics: a) 10 wt.% steam in feed; b) 30 wt.% steam in feed; c) 50 wt.% steam in feed; d) 70 wt.% steam in feed and e) 90 wt.% steam in feed.

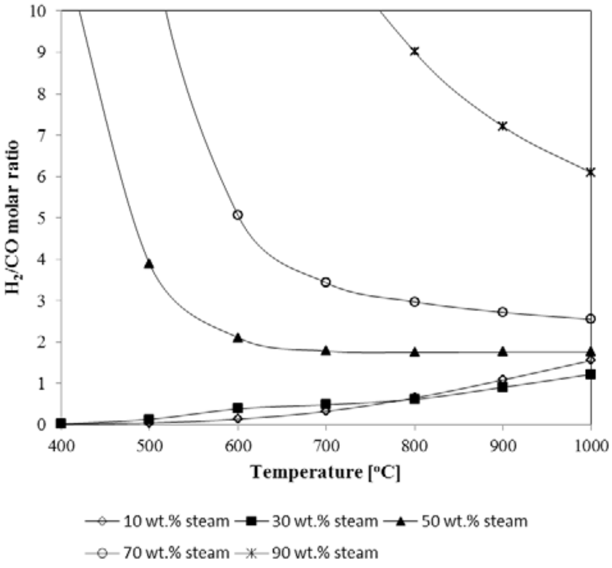

Fig. 3. H_2/CO ratio as function of steam contents in the feed and reaction temperature

REFERENCES

[1] N. Taufiqurrahmi, S. Bhatia, “Catalytic cracking of edible and non-edible oils for the production of biofuels”, *Energy Environ. Sci*., vol. 4, 2011, pp. 1087-1112

[2] M. Marquevich, X. Farriol, F. Medine, D. Montane, “Hydrogen production by steam reforming of vegetable oils using nickel-based catalysts”, *Ind. Eng. Chem. Res.,* vol. 40, 2001, pp. 4757-4766

[3] J. Gornay, L. Coniglio, F. Billaud, G. Wild, “Steam cracking and steam reforming of waste cooking oil in a tubular stainless steel reactor with wall effects”, *Energy Fuels*., vol. 23, 2009, pp. 5663

[4] ChemCad 6 Help and References manual, Chemstations, Inc. 11490,Westheimer Road, Suite 900, Houston, Texas 77077

[5] A.T.D. Butland, R. J. Maddison, “The specific heat of graphite and evaluation of measurements*”, J. Nuclear. Mat*., vol. 49, 1973/74, pp. 45-61

[6] L. Dandik, H.A. Aksoy, In Proceedings of the World Conference on Oilseed and Edible Oils Processing, S. S. Koseoglu, K.C. Rhee, R.F. Wilson, Eds.; AOCS Press: Champaign, 1998; Vol. 1, pp 126-129

[7] A.O. Adebanjo, A.K. Dalai, N.N. Bakhshi, “Production of diesel-like fuel and other value-added chemicals from pyrolysis of animal fat”, *Energy Fuels*., vol. 19, 2005, pp. 1735-1741