

# Energy requirements for vegetable oils to hydrogen process

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**Abstract**—This study has estimated the process energy requirements for producing H<sub>2</sub> from vegetable oils by steam reforming and has identified the most energy intensive step in the process in order to exploit opportunities for reducing energy requirements. A flowsheet was developed in ChemCad 6.4 and comprised three major steps: i) Steam reforming of vegetable oil, ii) Water-gas-shift (WGS) reaction and iii) CO<sub>2</sub> removal from the produced H<sub>2</sub>. The vegetable oil was modeled by triolein and steam-to-carbon (S/C) ratios of 3, 6 and 9 were considered. The energy required for H<sub>2</sub> production was estimated as ca. 111, 112 and 114 MJ/Kg for S/C ratios of 3, 6 and 9 respectively. The CO<sub>2</sub> removal process was found to be the most energy intensive accounting for ca. 60% of the process energy requirements. The major contributor to the high energy requirement for this section is CO<sub>2</sub> stripping.

**Key words**— Energy requirements, H<sub>2</sub> production, steam reforming, vegetable oil

## I. INTRODUCTION

PRODUCTION of H<sub>2</sub> from renewable sources currently receives more interest. H<sub>2</sub> derived from renewable sources is a cleaner energy source and can be used in fuel cells for electric power generation to meet future global energy needs [1]. Recent studies on H<sub>2</sub> production by reforming of glycerol [2-6] and vegetable oils [1, 7, 8] have been reported in literature. Interest in glycerol as a feedstock for H<sub>2</sub> production is mainly explained by the fact that it is a waste product of a biodiesel production plant. It is usually purified to some degree and sold to various refiners in order to improve the process economics but with more biodiesel production facilities coming on stream, glycerol price will continue to decrease. Markevich *et al.* [8] reported H<sub>2</sub> production by steam reforming of vegetable oils using Ni-based commercial and research catalysts. Their experimental results showed that oil conversion to gases and H<sub>2</sub> yields do not depend on the type of vegetable oil and hence indicated that the process might be suitable for producing H<sub>2</sub> from residual oils and fats from food processing in favour of the process economics. Pimenidou *et al.* [7] used NiO/Al<sub>2</sub>O<sub>3</sub> catalyst system for chemical looping reforming of waste cooking oil in packed bed reactor and reported a repeatable synthesis gas composition with H<sub>2</sub> selectivity very close to the equilibrium. Yenumala *et al.* [1] performed a thermodynamic analysis of the reforming of vegetable oil for H<sub>2</sub> production. They modeled the vegetable oil as a mixture

of tripalmitin, tristearin and trioleate, and reported optimum conditions for H<sub>2</sub> yield with very low methane selectivity. In another study [9] we have determined the effect of operating temperature, pressure and S/C ratios on H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub> and carbon formation during vegetable oil steam reforming for H<sub>2</sub> production.

Most studies on vegetable oils reforming for H<sub>2</sub> production focused more on kinetics and thermodynamic aspects and very little is known on the process energy requirements. Hence this study aims at i) estimating the process energy requirements for producing H<sub>2</sub> from vegetable oils by steam reforming; ii) identifying the most energy intensive step in the process in order to exploit opportunities for reducing energy requirements.

## II. METHODOLOGY

A process flowsheet was developed and simulated using ChemCad 6.4 simulation package to estimate the process energy requirements for producing H<sub>2</sub> from vegetable oils by steam reforming. The simulated flowsheet comprised three major steps: i) feed preparation and steam reforming of vegetable oil; ii) WGS reaction and iii) gas purification. 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 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 [10]. The selected possible components in the predicted equilibrium product included H<sub>2</sub>, CO, CO<sub>2</sub>, alkanes (C<sub>1</sub> to C<sub>15</sub>), olefins (C<sub>2</sub> to C<sub>15</sub>), 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. Operating conditions that minimize the formation of CH<sub>4</sub> and carbon determined in another study [9] were used: operating pressure of 1 bar and operating temperatures of 800, 900 and 1000°C for S/C ratios of 9, 6 and 3 respectively. The WGS reaction was used to convert the CO formed in the reforming reactor into more H<sub>2</sub>. This process was modeled by equilibrium conditions at high temperature (350°C) and low temperature (200°C). The gas from the WGS step was purified by condensing the unreacted steam out and by absorbing CO<sub>2</sub> using selexol. The property model used for the simulation

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was PSRK. The pressure drop in each unit operation was assumed negligible. The efficiencies for pump, compressors and expanders were assumed to be 75%.

### III. RESULTS AND DISCUSSION

The developed and simulated flowsheet for H<sub>2</sub> production by steam reforming of vegetable oil is presented in Fig. 1 and Table I reports mass and energy balances for the process that used a feed with an S/C ratio of 3. The vegetable oil and water were assumed to enter the process at 30°C (stream 1 and 2 respectively). Part of the energy of hot streams from the WGS and the reforming processes was respectively used to pre-heat and vaporise the feed water (in heat exchanger E-1 and E-2). Both steam and vegetable oil were pre-heated to the reforming temperature in a fired exchanger E-3 before entering the reformer R-1. The reformer temperature was 800, 900 and 1000°C for S/C ratios of 9, 6 and 3 respectively. Under these conditions CH<sub>4</sub> and carbon production were minimized as shown by the data for stream 7 in Table I where 0.02 kg/h of CH<sub>4</sub> and 7.70 kg/h of carbon were produced compared to 276, 927 and 1195 kg/h of H<sub>2</sub>, CO<sub>2</sub> and CO respectively. For mass balance purposes, a component separator S-1 was used to represent the process of carbon removal (not discussed in this study) from the reformer. The conversion of triolein in the reformer was complete. After cooling in heat exchanger E-2, the reformer outlet was sent to the high temperature (350°C) WGS stage (R-2) where about 86% of the CO formed during the reforming process was converted to H<sub>2</sub>. Further CO conversion was achieved in the low temperature WGS stage R-3 at 200°C after cooling in heat exchanger E-4. The two stages of the WGS process achieved a combined CO conversion of ca. 98.5%. After cooling to 40°C in exchanger E-1, the low temperature WGS reactor outlet was flashed in a drum F-1 at 1 bar for water removal. In this step about 73% of water was removed from the gas (compare stream 14 and 16 in Table I). After this step the gas pressure was increased 70 bar using a multistage compressor represented by a combination of compressors C-1, C-2, C-3 and intercoolers E-5 and E-6. The increase in gas pressure followed by cooling to 40°C in exchanger E-7 was performed for two reasons: i) allow more water removal in the flash drum F-2 and ii) improve CO<sub>2</sub> absorption in the downstream selexol process. About 99.5% of water was removed in drums F-1 and F-2 combined (compare stream 14 and 25). The gas was subsequently sent to the CO<sub>2</sub> absorption process where selexol was used as an absorbent. To simulate the selexol process, we slightly modified the Selexol Absorber and Stripper Combined Flash & Thermal Regeneration flowsheet in reference [11]. An absorption column T-1 with 8 stages at 70 bar was used for CO<sub>2</sub> absorption in selexol combined with flash drums F-3 and F-4, and a stripping column T-2 for selexol regeneration. The liquid outlet (stream 29) from the absorption column was expanded to 20 bar in a thermo-generator G-1 and flashed in drum F-3 where the gas outlet was re-compressed to 70 bar using a compressor C-4 and recycled to the absorption column to improve the process. This arrangement significantly reduced the loss of H<sub>2</sub> which was limited to ca. 0.4%. The selexol was further expanded to 10 bar in a thermo-generator G-2 and heated to 60°C in a heat exchanger E-8 before flashing in the drum F-4 where about

68% of CO<sub>2</sub> was removed from the absorbent. The selexol was further heated to 200°C using heat exchanger E-9 and sent to the stripping column T-2. This column was modeled by a shortcut design method using the Fenske expression. CO<sub>2</sub> was taken as the light key component with 99% split and selexol the heavy key with almost 0% split to distillate. A reflux to minimum reflux (R/R<sub>min</sub>) ratio of 1.2 was used. Under these operating conditions, about 20 separation stages with feed location around stage 14 were required. The selexol process achieved ca. 99.7% CO<sub>2</sub> removal in overall. A pump P-1 was used for selexol re-cycling to the absorption column via heat exchangers E-8, E-9 and E-10 where it was cooled down to 265, 206 and 40°C respectively before undergoing a refrigeration process to -1.1°C represented by the exchanger E-11. The purity of the H<sub>2</sub> produced (stream 26) was about 99.8 mol.%.

Table II summarizes the energy requirements for various sections of the process for S/C ratios of 3, 6 and 9 respectively. The WGS section had negative duties as the reaction is exothermic and therefore no additional energy was required. Part of the energy required by the process was generated by selexol expanders G-1 and G-2 and was entered with negative sign in Table II. The data show that the energy required to produce H<sub>2</sub> from steam reforming of vegetable oil slightly increases with an increase in S/C ratio. About 111, 112 and 114 MJ are required to produce 1 kg of H<sub>2</sub> from steam reforming of vegetable oil for S/C ratios of 3, 6 and 9 respectively. These energy requirements are high and opportunities for reducing them must be exploited. Fig. 2 shows the energy requirements per section of vegetable oil steam reforming process for S/C ratios of 3, 6 and 9. Gas purification is the most capital intensive and accounts for about 60% of energy requirements. A breakdown in energy required CO<sub>2</sub> removal for the process with S/C of 3 is presented in Fig. 3. These data are comparable to those for S/C ratios of 6 and 9 and show that the CO<sub>2</sub> stripping process is the most capital intensive and accounts for about 74% of the energy required for H<sub>2</sub> gas purification. This indicates that the CO<sub>2</sub> removal process must be the primary focus for reduction of energy requirements for the vegetable oil steam reforming process.



TABLE I

## MATERIAL AND ENERGY BALANCE FOR VEGETABLE OIL STEAM REFORMING PROCESS WITH S/C OF 3

Stream No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	
Temp C	30.0	30.0	99.6	450.6	328.8	1000.0	1000.0	1000.0	1000.0	350.0	350.0	200.0	200.0	40.0	40.0	40.0	244.0	105.0	324.9	110.0	367.4	40.0	40.0	40.0	
Pres bar	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	4.12	4.12	17	17	70	70	70	1	
Enth MJ/h	-2107.9	-55036.0	-51069.0	-43724.0	-45832.0	-38853.0	-30187.0	-40.6	-30200.0	-37545.0	-38966.0	-40572.0	-40787.0	-44754.0	-15210.0	-29544.0	-27873.0	-29075.0	-27193.0	-29069.0	-27151.0	-30725.0	-5423.7	-20634.0	
Total kmol/h	1.1	192.9	192.9	192.9	194.0	194.0	316.0	0.6	315.4	315.4	315.4	315.4	315.4	315.4	53.4	261.9	261.9	261.9	261.9	261.9	261.9	261.9	19.1	72.5	
Flow rates in kg/h																									
Carbon Dioxide	0.000	0.000	0.000	0.000	0.000	0.000	926.657	0.000	926.657	926.657	2541.426	2541.426	2776.291	2776.291	0.000	2776.291	2776.291	2776.291	2776.291	2776.291	2776.291	2776.291	2776.291	0.000	0.000
Methane	0.000	0.000	0.000	0.000	0.000	0.000	0.018	0.000	0.018	0.018	0.018	0.018	0.018	0.018	0.000	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0.000
Water	0.000	3475.000	3475.000	3475.000	3475.000	3475.000	2069.607	0.000	2069.607	2069.607	1408.619	1408.619	1312.480	1312.480	962.895	349.584	349.584	349.584	349.584	349.584	349.584	349.584	349.584	343.361	1306.256
Hydrogen	0.000	0.000	0.000	0.000	0.000	0.000	275.638	0.000	275.638	275.638	349.599	349.599	360.357	360.357	0.000	360.357	360.357	360.357	360.357	360.357	360.357	360.357	360.357	360.357	0.000
Carbon Monoxide	0.000	0.000	0.000	0.000	0.000	0.000	1195.398	0.000	1195.398	1195.398	167.684	167.684	18.206	18.206	0.000	18.206	18.206	18.206	18.206	18.206	18.206	18.206	18.206	18.206	0.000
triolen	1000.000	0.000	0.000	0.000	999.998	999.998	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Carbon	0.000	0.000	0.000	0.000	0.000	0.000	7.700	7.700	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
Selexol (TM)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
Stream No.	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47		
Temp C	40.0	-1.2	-1.1	-1.1	7.8	5.8	5.8	200.5	5.8	5.2	60.0	60.0	60.0	200.0	98.6	383.7	389.4	265.1	206.2	206.2	206.2	40.0	-1.1		
Pres bar	70	70	70	70	70	20	20	70	20	10	10	10	10	10	10	10	70	70	70	70	70	70	70		
Enth MJ/h	-25301.0	-329.3	-2.3	-17033.0	-42799.0	-42972.0	-817.5	-794.5	-42154.0	-42189.0	-36730.0	-16906.0	-19824.0	-7198.6	-7892.4	18519.0	19140.0	6514.8	1055.8	0.1	1055.7	-13565.0	-17031.0		
Total kmol/h	242.8	178.9	0.0	150.4	219.1	219.1	4.8	4.8	214.4	214.4	214.4	43.7	170.6	170.6	20.2	150.4	150.4	150.4	150.4	0.0	150.4	150.4	150.4		
Flow rates in kg/h																									
Carbon Dioxide	2776.290	4.638	0.000	8.912	2870.905	2870.907	90.341	90.341	2780.566	2780.566	2780.566	1889.293	891.273	891.273	882.361	8.913	8.913	8.913	8.913	0.001	8.912	8.912	8.912		
Methane	0.018	0.016	0.000	0.000	0.003	0.003	0.001	0.001	0.002	0.002	0.002	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000		
Water	6.224	0.008	0.000	0.034	6.296	6.296	0.046	0.046	6.251	6.251	6.251	2.805	3.446	3.446	3.412	0.034	0.034	0.034	0.034	0.000	0.034	0.034	0.034		
Hydrogen	360.357	359.049	0.000	0.000	6.739	6.739	5.431	5.431	1.308	1.308	1.308	1.288	0.020	0.020	0.020	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000		
Carbon Monoxide	18.206	17.934	0.000	0.000	0.799	0.799	0.528	0.528	0.271	0.271	0.271	0.266	0.005	0.005	0.005	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000		
triolen	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000		
Carbon	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000		
Selexol (TM)	0.000	0.000	5.441	40000.012	40000.012	40000.012	0.000	0.000	40000.012	40000.012	40000.012	0.041	40000.000	40000.000	0.400	39999.574	39999.574	39999.582	39999.570	4.999	39994.570	39994.570	39994.570		

TABLE II  
SUMMARY OF ENERGY REQUIREMENTS FOR VEGETABLE OIL STEAM REFORMING TO PRODUCE H<sub>2</sub>

Operation description	Equipment symbol	Required energy [MJ/h]		
		S/C ratio = 3	S/C ratio = 6	S/C ratio = 9
<b>Reforming process</b>				
Feed heating (Fired heater)	E-3	6979.4	8446.5	9932.3
Reforming process	R-1	8665.7	7777.5	7033.8
<b>WGS process</b>				
HT WGS reaction	R-2	-	-	-
LT WGS reaction	R-3	-	-	-
<b>Gas purification</b>				
Absorber feed gas compression (stage 1)	C-1	1670.9	1676.5	1672.3
Absorber feed gas compression (stage 2)	C-2	1882.0	1888.3	1883.6
Absorber feed gas compression (stage 3)	C-3	1918.4	1924.8	1920.0
Absorber recycle gas compression	C-4	23.0	23.2	23.1
CO <sub>2</sub> stripping	T-2	17958.9	17958.9	17958.9
Selexol recycling	P-1	621.0	621.0	621.0
Selexol refrigeration	E-11	191.2	191.2	191.2
Expander 1 (generated energy)	G-1	-172.5	-172.7	-172.6
Expander 2 (generated energy)	G-2	-35.0	-35.0	-35.0
<b>Process energy requirements</b>		<b>39703.0</b>	<b>40300.3</b>	<b>41028.6</b>
<b>H<sub>2</sub> production [Kg/h]</b>		<b>359.0</b>	<b>360.5</b>	<b>359.7</b>
<b>CO<sub>2</sub> production</b>		<b>2776.3</b>	<b>2802.4</b>	<b>2795.8</b>
<b>Energy required per kg of H<sub>2</sub> [MJ/Kg]</b>		<b>110.6</b>	<b>111.8</b>	<b>114.1</b>

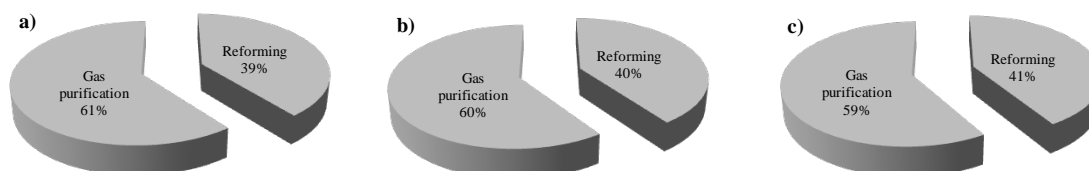


Fig. 2. Energy requirements per process section

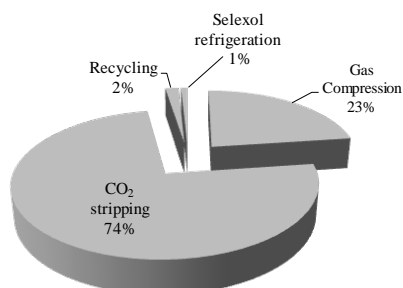


Fig. 3 Energy requirements breakdown for the H<sub>2</sub> gas purification process.

## IV. CONCLUSION

The production of H<sub>2</sub> from vegetable oil steam reforming was modeled by a simulation flowsheet in ChemCad 6.4 and comprised three major steps: i) Steam reforming of vegetable oil, ii) WGS reaction and iii) CO<sub>2</sub> removal from the produced H<sub>2</sub>. The energy required for H<sub>2</sub> production was ca. 111, 112 and 114 MJ/Kg for S/C ratios of 3, 6 and 9 respectively. The CO<sub>2</sub> removal process was found to be the most energy intensive accounting for ca. 60% of the process energy requirements. The major contributor to this high energy requirement is the CO<sub>2</sub> stripping. CO<sub>2</sub> removal process must receive more attention in an attempt to reduce the process energy requirements.

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