

## KINETICS, CATALYSIS, AND REACTION ENGINEERING

## Steam Reforming of Sunflower Oil for Hydrogen Production

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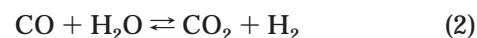
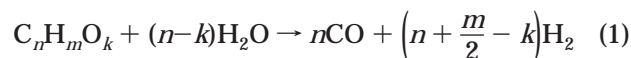
We studied the production of hydrogen by the catalytic steam reforming of sunflower oil, a renewable resource that is already used as feedstock for producing biodiesel. The study was performed in a fixed-bed reactor with a commercial nickel-based catalyst for steam-reforming naphtha. Steam-to-carbon (S/C) ratios of 3, 6, and 9 and catalyst temperatures from 550 to 880 °C were tested at a constant space velocity ( $M_{C1}HSV$ ) of  $410 \text{ mol}_{\text{carbon}} \text{ h}^{-1} \text{ L}_{\text{catalyst}}^{-1}$ , equivalent to a gas hourly space velocity ( $G_{C1}HSV$ ) of  $9150 \text{ h}^{-1}$ . Sunflower oil was completely converted to hydrogen, methane, and carbon oxides, except for the runs performed at the lowest temperatures and an S/C ratio of 3. The hydrogen yield ranged from 72% to 87% of the stoichiometric potential, depending on the steam-to-carbon ratio and the catalyst temperature, which governed the equilibrium among gas species. Thermal cracking of the oil in the gas-phase was a competing process during steam reforming, especially above 650 °C where it converted fatty acids to a wide array of products, including ethylene and aromatics. Cracking products were subsequently converted to hydrogen and carbon oxides by the catalytic steam-reforming reaction. A gradual deactivation of the catalyst by carbon deposition was observed in long-duration reforming experiments, although catalyst activity was restored after steaming at 850 °C for 3 h.

## Introduction

Hydrogen is an industrial commodity that is mainly used for synthesizing ammonia and methanol, refining petroleum, and processing petrochemicals. Besides these well-established applications, hydrogen has great potential as a fuel and energy carrier. A sustainable energy system based on hydrogen is envisaged as a probable scenario for the mid-term future, mainly through the intensive use of fuel cells.<sup>1</sup> Although the advantages of hydrogen over fossil fuels are unquestionable when considered at the local level, producing hydrogen by the current methods may have disadvantages which outweigh the benefits when considered on a global level. Most hydrogen is produced on an industrial scale from natural gas, LPG, and naphtha by catalytic steam reforming, and from heavy oil fractions by partial oxidation.<sup>2</sup> Both processes are well established. The first one is the most economical for large-scale hydrogen production.<sup>3</sup> Steam reforming of hydrocarbons is performed in fixed-bed tubular reactors with nickel-based catalysts. In standard operation conditions the mixture of hydrocarbon and steam enters the catalyst bed at a temperature around 450–600 °C and the products leave the reactor at 790–850 °C. The reactor pressure ranges from 20 to 40 bar, depending on the final use of the produced hydrogen.<sup>4,5</sup> Typical steam-to-carbon molar ratios range from 2.5 to 6.5, depending on the feedstock, the catalyst, and the final product required (hydrogen, CO/H<sub>2</sub> mixture for metha-

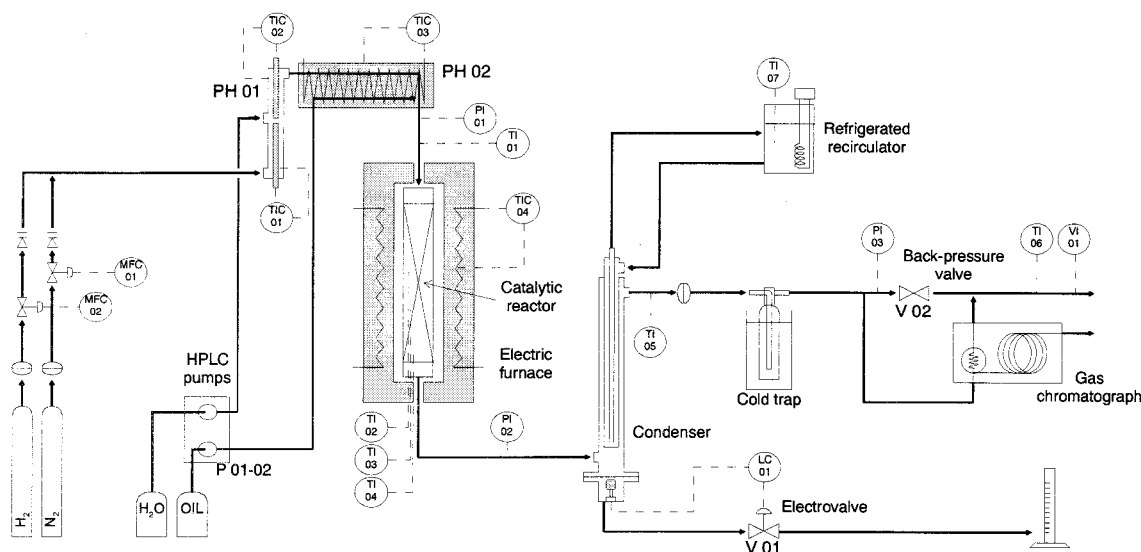
nol synthesis or hydrogen for ammonia synthesis). If the desired product is hydrogen, steam-to-carbon ratios above 5 are used.<sup>6</sup> Methane-equivalent gas hourly space velocity ( $G_{C1}HSV$ ) for naphtha reforming typically ranges from 700 to 2000  $\text{h}^{-1}$ .<sup>6</sup>

In the steam-reforming reaction the organic molecule ( $C_nH_mO_k$ ) is adsorbed onto the nickel surface, where it completely converts to carbon monoxide and hydrogen according to reaction (1). Carbon monoxide and hydrogen then react to form methane and carbon dioxide by the equilibrium reactions (2) and (3). Thus, the composition of the gas mixture at the reformer outlet almost reaches equilibrium.<sup>7</sup> Hydrogen and carbon oxides are the predominant species at the typical operating conditions for steam-reforming reactors, while the methane concentration is below 2 mol % at the catalyst temperatures and pressures at the exit of the reactor. To increase the yield of hydrogen, carbon monoxide in the reformer gas is further converted to carbon dioxide and hydrogen in downstream water shift reactors (reaction (2)). Typically, less than 0.4 mol % of carbon monoxide is encountered in the gas after the low-temperature water shift reactor.<sup>7</sup>



Carbon dioxide is generated in large amounts in the production of hydrogen by the steam reforming of hydrocarbons, not only as a reaction product but also

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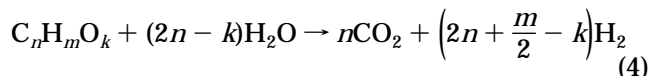


**Figure 1.** Fixed-bed catalytic reactor.

in the flue gas of the reformer furnace. The environmental benefits of a hydrogen-based energy system may therefore be questionable if the demand for hydrogen has to be covered by intensive use of fossil resources because this process is clearly a net contributor to carbon dioxide emissions. Depending on the efficiencies of hydrogen production, distribution, and use, the hydrogen-based scenario may be even less favorable environmentally than the direct use of fossil fuels. We think that the true potential of a hydrogen-based energy system may only be achieved if hydrogen is made available from renewable resources. Over the past few decades lignocellulosic biomass has been suggested as being one of the main renewable energy sources because it can reduce emissions of carbon dioxide and make us less dependent on fossil fuels for generating power or for transport.<sup>8,9</sup> Hydrogen may be produced from lignocellulosics by two different thermochemical methods: gasification of biomass followed by water shift<sup>10,11</sup> or fast pyrolysis of biomass followed by steam reforming of the pyrolytic oil (bio-oil) or its fractions.<sup>12</sup> Both methods have similar potential for producing hydrogen.<sup>13,14</sup> Laboratory studies of bio-oil fractions and model compounds have concluded that they can be effectively converted to hydrogen using commercial catalysts for the steam reforming of naphtha.<sup>14–17</sup>

Vegetable oils and fats are a particular form of biomass that has attracted considerable interest as renewable feedstock for energy and chemicals. Vegetable oils are a mixture of fatty esters of glycerol that have molecular weights of around 800–900 and are made up of a relatively low number of fatty acids. For example, the main fatty acids in sunflower oil are linoleic acid (73.7%, C18:2), oleic acid (16.9%, C18:1), palmitic acid (C16:0), and stearic acid (C18:0).<sup>18</sup> Rapeseed, canola, and sunflower oils have been studied for energy applications in the transportation sector as a fuel for diesel engines (biodiesel)<sup>19–23</sup> and also for the production of olefins and other hydrocarbons by pyrolysis<sup>24,25</sup> and catalytic cracking.<sup>26</sup> We think that vegetable oils are a promising feedstock for the production of hydrogen because of their low oxygen content and subsequent high-potential yields of hydrogen. The maximum hydrogen yield that may be obtained for a specific feedstock in an industrial steam-reforming plant (reformer + water shift reactors) can be evaluated from

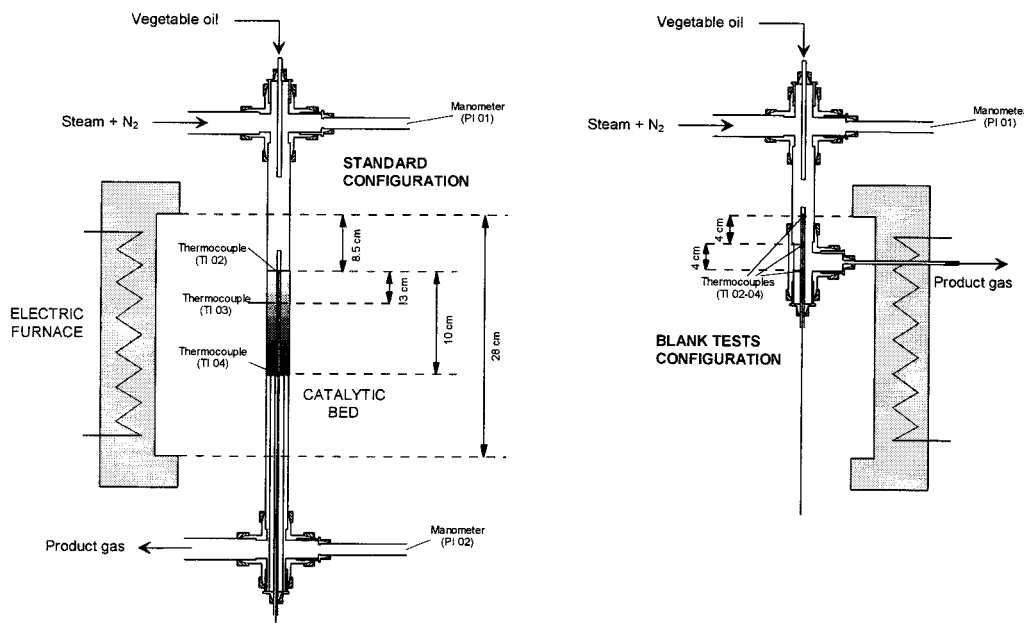
eq 4, which combines reactions (2) and (3), assuming that they are completely displaced to the formation of hydrogen. In this case, the potential hydrogen yield is  $(2 + m/2n - k/n)$  mol of  $H_2$ /mol of carbon in the organic molecule. Although actual yields are slightly lower because of the small amount of methane that leaves the reformer, the potential yield of hydrogen calculated from eq 4 provides the maximum theoretical yield of hydrogen attainable for a specific feedstock by a steam-reforming process. The presence of oxygen in molecules with an equal number of carbon and hydrogen atoms reduces the stoichiometric yield of hydrogen by a factor of  $(k/n)$ . Therefore, on a mass basis, 1000 kg of the sunflower oil used in this study ( $C_{18}H_{34.4}O_{2.1}$ ) could potentially yield 360 kg of hydrogen gas, while the same amount of water-free bio-oil from biomass pyrolysis ( $CH_{1.33}O_{0.53}$ )<sup>27</sup> can produce only 196 kg of hydrogen gas, that is, only 55% of the potential yield from sunflower oil. In comparison, potential yields for methane and naphtha (e.g.,  $C_7H_{16}$ ) are 500 and 440 kg of hydrogen/1000 kg of feed, respectively. This paper reports the



production of hydrogen from sunflower oil using a commercial catalyst and process conditions for steam-reforming naphtha. We performed a systematic study at the bench scale to determine the effect of the reforming temperature and steam-to-carbon ratio on the yield of hydrogen and the composition of the produced gas. Long-duration tests were conducted to study catalyst deactivation and regeneration, and a series of blank tests were done to determine the extent of thermal cracking of sunflower oil in the reactor freeboard above the catalyst bed. Sunflower oil has been selected as a prototype vegetable oil. Because of the similitude in composition of most vegetable oils produced in temperate climates, such as rapeseed, soybean, canola, or maize, the behavior of sunflower oil during steam reforming may be extended to other oils, at least qualitatively.

## Materials and Methods

**Reactor.** This study was carried out in the bench-scale reactor schematized in Figure 1. The unit consists



**Figure 2.** Arrangement of the catalyst inside the reactor tube.

of a fixed-bed catalytic reactor with downdraft flow, constructed with a 12.7-mm ( $1/2$ -in.) o.d. 316-L stainless steel tube. The reactor is externally heated with an electric furnace that can operate at temperatures up to 1100 °C. The total length of the heating section of the furnace is 28 cm. The catalyst is held up by a metallic grid and placed inside the reactor tube as shown in Figure 2. The temperature of the catalyst bed is measured at three different heights by three thermocouples (type K, 0.5-mm o.d.), which are placed inside a 3.18-mm ( $1/8$ -in.) o.d. 316-L stainless steel sheath along the center of the reactor. The first thermocouple (TI 02) measures the temperature at the beginning of the bed, the second (TI 03) at  $1/3$  of the bed height, and the last one (TI 04) at the bed outlet. Figure 2 also depicts the position of the three thermocouples for the blank tests that were conducted to establish the extent of thermal cracking in the freeboard of the fixed-bed reactor. A shorter reactor with rapid product quenching, which simulated the freeboard of the catalytic reactor, was constructed and used to perform the thermal-cracking tests.

Water and sunflower oil are pumped at room temperature by two high-precision HPLC-metering pumps. Water is vaporized in a preheater (PH 01), which consists of two electric heaters of 500 W held at 400 °C. Nitrogen is mixed with steam in the preheater and used as a carrier gas and internal standard for gas analysis by gas chromatography. The flow rate of nitrogen is regulated by a mass flow controller (MFC 01). The resulting mixture flows to the reactor through a heated line (PH 02). Sunflower oil is vaporized and mixed with steam and nitrogen at the entrance to the reactor tube. One thermocouple (TI 01) is placed in the mixing point to measure the temperature of the mixture before it enters the reactor, and a manometer and a pressure transducer (PI 01) measure the pressure at the same point. Another measure of pressure (PI 02) is taken at the reactor outlet to determine the differential pressure through the catalyst bed. The gas produced in the reactor passes through the external part of a vertical concentric-pipe type condenser, in which a cold mixture of water and propylene glycol circulates continuously

in countercurrent flow through the inner pipe. Excess steam is recovered at the bottom of the condenser, where a float switch is installed to pilot an electric valve (V 01) to keep the level of liquid constant. The amount of water condensed is measured in a graduated cylinder. The gas then flows through a cold trap that practically condenses all the remaining water. A portion of the dry gas stream passes through the gas chromatograph sample loop, while the rest goes through a back pressure regulator (V 02) which controls the pressure of the system. The volumetric flow rate of dry gas is measured at atmospheric pressure with a turbine-type meter (VI 01), and the temperature of the gas is also recorded to calculate the mass flow rate of gas. Temperatures in the bed (TI 02–04), pressures (PI 01–03), and gas flow rate (VI 01) are registered by a PC-based data acquisition system and continuously monitored.

**Product Analysis.** The composition of the gas was determined by an on-line gas chromatograph (Hewlett-Packard 5890) equipped with two columns and a thermal conductivity detector. Column 1 was a Chromosorb 102 packed column (3.6 m; 3.18-mm ( $1/8$ -in.) o.d.; 60/80 mesh) while column 2 was packed with molecular sieve 13X (2 m; 3.18-mm ( $1/8$ -in.) o.d.; 80/100 mesh). The first column separates carbon dioxide from the other gases, while the second column separates hydrogen, nitrogen, methane, and carbon monoxide. A pneumatic 10-way valve (VALCO A-4C10UWT) was used to inject the sample through a 1-mL sample loop and to switch the columns during analysis.

A Carboxen 1000 packed column (1.5 m; 3.18-mm ( $1/8$ -in.) o.d.; 60/80 mesh) was used for the thermal-cracking tests because it allows hydrogen, nitrogen, methane, carbon dioxide, carbon monoxide, acetylene, ethylene, ethane, and a C3 peak (propane and propylene) to be separated simultaneously. This column was also used routinely for the long-duration tests. The fraction of organic liquid recovered from the thermal-cracking experiments was analyzed qualitatively by GC-MS using a Hewlett-Packard 5890 chromatograph with a 5989A mass spectrometer system.

**Materials.** This study used a sample of commercial sunflower oil. The elemental composition of the oil was



**Table 1. Thermal Cracking of Sunflower Oil in the Reactor Freeboard: Experimental Conditions, Gas Flow Rate and Composition, and Percentage of Carbon Converted to Gases (CO, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>, and C<sub>3</sub><sup>+</sup>)<sup>a</sup>**

furnace	temperatures (°C)			residence time (ms)	gas flow rate (SLM)	gas composition (%)							carbon in gases (% feed)
	TI 02'	TI 03'	TI 04'			CO	CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> <sup>+</sup>	
900	588	762	817	42	0.23	23.6	8.6	17.1	1.3	35.0	1.8	12.6	8.8
800	504	657	715	46	0.15	18.1	10.7	13.4	0.6	39.1	3.2	14.9	5.8
700	430	550	611	51	0.06	18.4	13.7	12.5	n.d.	36.4	5.1	13.8	2.3
600	382	471	520	60	0.01	13.1	37.9	13.1	n.d.	25.7	n.d.	10.3	0.4

<sup>a</sup> All experiments performed at a steam-to-carbon ratio of 6 and the same oil flow rate of the reforming experiments.

**Table 2. Steam Reforming of Sunflower Oil: Experimental Conditions and Percentage of Carbon Converted to Gases (CO<sub>2</sub>, CO, and CH<sub>4</sub>)<sup>a</sup>**

run no.	steam-to-carbon ratio (mol/mol)	average temperatures (°C)				run time (min)	carbon in gas products (% feed)
		furnace	TI-02	TI-03	TI-04		
15	9	900	778	797	892	55	99.9
22			794	839	899	55	100.9
28			812	852	920	52	99.8
23		800	737	729	801	54	100.6
29			742	731	814	58	99.4
24	6	700	665	668	685	57	97.7
30			660	665	686	60	91.3
35		600	503	570	616	55	95.1
16		900	803	860	905	55	94.8
31			841	863	920	54	97.3
17	3	800	738	723	807	54	94.0
32			770	743	817	59	96.4
18		700	679	664	687	59	92.7
33			695	683	687	53	92.3
34		600	548	582	631	60	93.5
19	6	900	811	879	908	53	96.4
25			812	871	900	57	102.0
20		800	750	732	812	54	95.6
26			764	732	805	54	100.2
21		700	691	674	692	54	94.6
27	9		708	681	697	54	100.1
36		600	561	567	602	40	68.5

<sup>a</sup> All experiments performed at a space velocity ( $M_{C1}HSV$ ) of 410 mol<sub>carbon</sub> h<sup>-1</sup> L<sub>catalyst</sub><sup>-1</sup>, equivalent to a gas hourly space velocity ( $G_{C1}HSV$ ) of 9150 h<sup>-1</sup>.

determined with a Carlo Erba EA1108 analyzer. The weight percentages of the oil components were 75.9 ± 0.3 of carbon, 12.1 ± 0.2 of hydrogen, and 12.0 ± 0.4 of oxygen. This corresponds to an average formula of C<sub>18</sub>H<sub>34.4</sub>O<sub>2.1</sub>.

In this investigation we used a commercial catalyst (United Catalysts G-90C) containing 15% of nickel supported on a ceramic carrier (70%–76% Al<sub>2</sub>O<sub>3</sub> and 5%–8% CaO) for the steam reforming of naphtha. The catalyst was crushed from its original size (rasching ring shape; 5/8-in. o.d., 5/16-in. i.d., and 5/8-in. length) into smaller particles (1 < dp < 2 mm). Around 10 g of catalyst was packed into the reactor. The fresh catalyst was reduced at 600 °C for 4 h under a constant flow of 0.8 SLM (standard liters minute) of an equimolar mixture of hydrogen and nitrogen.

**Operating Conditions.** A systematic study of the influence of temperature and steam-to-carbon ratio was performed at constant near-atmospheric pressure. Experiments were performed at steam-to-carbon ratios of 3, 6, and 9 and furnace temperatures of 600, 700, 800, and 900 °C, which resulted in catalyst temperatures of between 550 and 880 °C (Table 2). This range of temperature is relevant for steam-reforming reactions.<sup>7,14</sup> We have used a definition of space velocity based on the moles of carbon present in the reactor feed.<sup>14</sup> Units for the hourly space velocity, denoted  $M_{C1}HSV$ , are moles of carbon in the feed per volume of catalyst (in L) and time (in h). We have used a space

velocity ( $M_{C1}HSV$ ) of 410 mol<sub>carbon</sub> h<sup>-1</sup> L<sub>catalyst</sub><sup>-1</sup> for all the experiments, which is equivalent to a gas hourly space velocity ( $G_{C1}HSV$ ) of around 9150 h<sup>-1</sup>. This high space velocity, between 4 and 10 times higher than that used in studies of the steam reforming of hydrocarbons and bio-oil model compounds,<sup>14,17</sup> was selected to test the performance of the catalyst under severe reaction conditions. Short experiments were conducted for 1 h under steady-state conditions and duplicated to test reproducibility of the results. A single load of catalyst was used for the short experiments, with a total time on stream of around 60 h at several combinations of temperatures and steam-to-carbon ratios. Three experiments were performed daily, which accounting for the stabilization intervals when changing operating conditions, represented around 6 h of continuous operation. Before the unit was shut down, the catalyst was steamed at 850 °C to remove any possible carbon deposits and kept overnight at 400 °C under a constant flow of 0.1 SLM of nitrogen. Long-duration steam-reforming experiments were performed for 50 h to test catalyst deactivation and regeneration.

Thermal cracking in the reactor freeboard was studied using the modified reactor setup schematized in Figure 2. Cracking experiments were performed at a steam-to-carbon ratio of 6 and the same furnace temperatures (600, 700, 800, and 900 °C) and oil feed rate as those used for the steam-reforming experiments.

## Results and Discussion

**Extent of Thermal Cracking.** Steam reforming is a strongly endothermic reaction process that requires high catalyst temperatures, that is, well over 500 °C, to operate satisfactorily. Homogeneous thermal cracking of naphtha in the gas phase occurs as a competing process during steam reforming. Cracking is especially important in the initial section of the bed where naphtha reaches 625–675 °C and its partial pressure is still high, resulting in similar rates for the cracking and reforming reactions.<sup>28,29</sup> Thermal cracking is also a competing and unavoidable process during steam reforming of vegetable oils. Thermal cracking of vegetable oils, either in the absence or in the presence of steam, has been studied for the production of olefins and other valuable hydrocarbons,<sup>24,25</sup> and a general reaction pathway has been established.<sup>25</sup> We conducted several cracking experiments at reactor temperatures equivalent to those of the reforming experiments, to determine the extent of thermal cracking in the freeboard of our reactor system. Table 1 shows the results at a steam-to-carbon ratio of 6.

Very low conversions, of the carbon fed to the system, to gas products was observed below 650 °C, indicating that thermal cracking was minimal. The gas contained carbon dioxide, carbon monoxide, and ethylene. Thermal cracking of vegetable oils starts at 250–350 °C by cleavage of the ester bonds to yield free fatty acid chains. At higher temperatures fatty acids decompose by de-

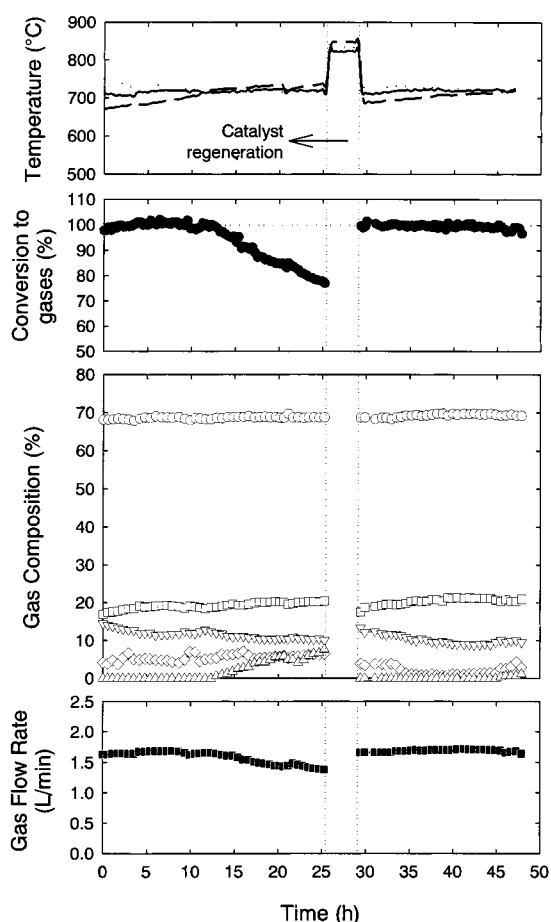
carboxylation and decarbonylation to saturated and unsaturated hydrocarbons, liberating carbon oxides. These hydrocarbons are then further converted by ethylene elimination, isomerization, and hydrogen-transfer reactions to yield ethylene, propylene, and other small hydrocarbons.<sup>25</sup> Qualitative GC-MS analysis of the liquid fraction from experiments below 650 °C revealed a main peak of the mixture of linoleic, oleic, and stearic acids (C18) and a much smaller peak of palmitic acid (C16). This shows that C–C bond cleavage of the unsaturated fatty acid chains did not take place to a detectable degree at these conditions of temperature and heating time.

The amount of carbon recovered in the gas products was 5.8% when the feed was heated to 715 °C in 46 ms. Carbon monoxide, ethylene, and methane were the main components of the gas, while there was evidence of extensive cracking of the organic liquid when it was analyzed by GC-MS. The peaks of C18 and C16 fatty acids almost disappeared and a wide array of hydrocarbon products were detected. Short-chain oxygenated hydrocarbons were observed (C10 and smaller), which are formed by the C–C scission of the unsaturated fatty acid chains.<sup>25</sup> Cycloolefins and aromatics were also present in the cracking products. Results were similar when the oil was heated to 817 °C in 42 ms. Nearly 9% of the carbon was recovered in the gas products. Fatty acids were not detected in the liquid products by GC-MS analysis, which indicates that cracking of the oil was complete. The yields and variety of aromatic products increased, and benzene and its derivatives, e.g., methyl- and ethylbenzene, and naphthalene were dominant among the liquid products.

Previous results indicate that the fatty acids liberated by thermal decomposition of the vegetable oil will be converted by steam reforming predominantly over thermal cracking if the oil feed is maintained below 650 °C for short heating times. Above this temperature the fatty acid chains will be extensively cracked in the gas phase, and the cracking products will be those converted to hydrogen by the steam-reforming reactions.

**Steam Reforming: Long-Duration Tests.** Carbon deposition on the catalyst surface is one of the main problems of steam-reforming hydrocarbons.<sup>6,7,30,31</sup> For biomass-derived feedstocks, it is known that carbon may form and deactivate the catalyst after a few hours of operation during the steam reforming of bio-oil, but these carbon deposits are easily removed by steaming while the catalyst recovers the initial activity.<sup>14,32</sup> Steam-reforming reactions (eqs 1–3) compete with the reactions that lead to the formation of carbon on the active surface and to the deactivation of the catalyst. For a specific steam-reforming catalyst, the relative rate among both processes depends on the availability of steam on the surface to complete reaction (1), the temperature of the catalyst, and the structure of the organic molecule. Furthermore, carbon deposition on the catalyst surface may be accelerated by the formation of carbon precursors by homogeneous thermal cracking in the gas phase.

We conducted long-duration tests to assess catalyst deactivation during the steam reforming of sunflower oil and the possibility of regenerating the deactivated catalyst by steaming. The tests were conducted at reaction conditions proven to be efficient for steam-reforming bio-oil and at space velocities that ensured complete conversion of the feed.<sup>14</sup> Figure 3 shows results

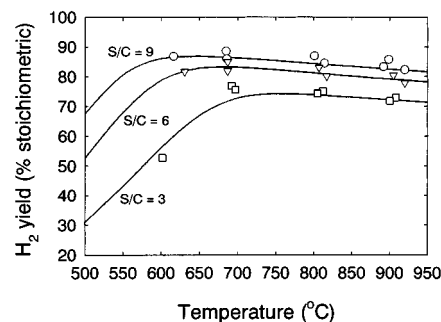


**Figure 3.** Steam reforming of sunflower oil in a long-duration experiment at an S/C ratio of 6. Temperature profiles in the catalyst bed (TI-02, —; TI-03, ---; TI-04, ...), conversion of carbon to carbon-containing gases (●), gas composition ( $\text{H}_2$ , ○;  $\text{CO}_2$ , □; CO, ▽;  $\text{CH}_4$ , △; and  $\text{C}_2\text{H}_4$ , ▴) and gas flow rate (■). See text for details on regeneration (steaming).

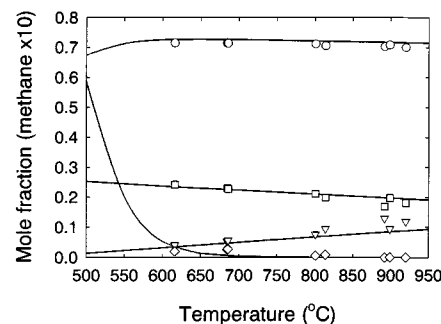
of the steam reforming of sunflower oil at 720 °C and a steam-to-carbon ratio of 6. The space velocity ( $M_{\text{C1}}\text{HSV}$ ) for this experiment was  $410 \text{ mol}_{\text{carbon}} \text{ h}^{-1} \text{ L}_{\text{catalyst}}^{-1}$ , which is equivalent to a  $G_{\text{C1}}\text{HSV}$  of around  $9150 \text{ h}^{-1}$ , that is, 9 times higher than that in the steam reforming of bio-oil and its model compounds.<sup>14,17</sup> Results show a very stable operation for nearly 14 h with 100% of the carbon fed to the system recovered in the output gas. The flow rate of gas was also constant during this period, while gas composition varied slightly: the concentrations of hydrogen, carbon dioxide, and methane increased and that of carbon monoxide decreased. This may have been due to the continual decrease in the temperature of the catalyst at the exit of the bed during the experiment (TI 04, from 750 to 700 °C), which displaced the chemical equilibrium among gas species. This decrease in temperature points to catalyst deactivation. When the feed of sunflower oil started, the temperature in the first section of the bed (TI 02 and TI 03), because of the endothermic character of the overall reaction, dropped suddenly, but the temperature at the bed exit (TI 04) did not change. This shows that all the oil was converted in the initial section of the bed. As the catalyst started to lose activity, more and more catalyst was needed to completely convert sunflower oil, until the “reaction front” reached the catalyst located at the bed exit. At this point, around 14 h after the oil feed was started, the temperature of the catalyst was uniform throughout the catalyst bed and ethylene was

detected in the outlet gas. From then on, the gas flow rate and the percentage of carbon recovered in the outlet gas started to drop, while the concentration of ethylene increased steadily. After 25 h the feed of sunflower oil was stopped, and the catalyst was steamed for 3 h at 850 °C to remove carbon deposits. As we showed in the previous section, ethylene is one of the main gaseous products formed by thermal cracking of sunflower oil. The formation of carbon on nickel catalysts from ethylene is much faster than that from other hydrocarbons such as aromatics and alkanes,<sup>7</sup> so the deactivation of the catalyst in our case is probably accelerated by the ethylene, resulting from the competing thermal-cracking reactions. Carbon balances show that the carbon that was not recovered in the gas products was collected in the liquid byproducts that were condensed together with steam at the reactor outlet. These byproducts began to appear in the water shortly after ethylene was detected in the outlet gas. Consequently, only a small amount of carbon accumulated on the catalyst surface during the experiment, and the catalyst could be regenerated by steam gasification of the carbon deposits. After steaming, the catalyst temperature was lowered again to 720 °C and the oil feed restarted. Carbon conversion to gases again reached 100% while the gas flow rate, gas composition, and catalyst temperatures regained the values they had at the beginning of the experiment. The catalyst bed maintained complete conversion for more than 16 h until ethylene appeared again in the outlet gas. The evolution of the bed temperatures and gas composition during this interval was identical to that for the first part of the experiment, which proves that steaming was efficient for restoring catalyst activity.

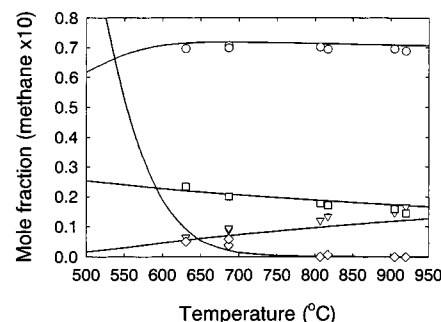
**Steam Reforming: Effect of Operating Conditions.** We conducted a systematic series of short experiments. Each experiment lasted roughly 1 h at stable conditions. Between one experiment and the next we varied temperature and/or steam-to-carbon ratios to determine how this affected hydrogen yield. The results were compared with the hydrogen yield and gas composition that are expected for each set of conditions from equilibrium calculations. Table 2 shows the operating conditions for the series of short experiments and the percentage of carbon converted to gas products (CO<sub>2</sub>, CO and CH<sub>4</sub>). All experiments were conducted at a space velocity ( $M_{C1}HSV$ ) of 410 mol<sub>carbon</sub> h<sup>-1</sup> L<sub>catalyst</sub><sup>-1</sup> ( $G_{C1}HSV$  of 9150 h<sup>-1</sup>). Conversion of carbon to gases was complete at all conditions, except when catalyst temperatures were below 600 °C at a steam-to-carbon ratio of 3. Carbon conversion to gases was less than 69% for this experiment, condensable organic products were collected in the condenser at the reactor outlet, and trace amounts of ethylene were detected in the gas. For all other experiments carbon balances higher than 95% were usual and water collected in the condenser was free of organic compounds, which indicates complete conversion of sunflower oil to gases. Figure 4 plots the experimental yield of hydrogen and the yield from the equilibrium calculations for the steam reforming of sunflower oil at the three values of steam-to-carbon ratios versus the temperature at the outlet of the bed (TI 04). Both yields are expressed as percentages of the maximum theoretical yield of hydrogen calculated from eq 4. Our experimental results agree with the equilibrium calculations for this system. Hydrogen yields from 80% to 87% are obtained at a steam-to-carbon ratio above 6. Temperature has little influence on hydrogen



**Figure 4.** Steam reforming of sunflower oil: comparison of experimental hydrogen yields and thermodynamic equilibrium calculations for the experiments performed at steam-to-carbon ratios (S/C) of 9,  $\circ$ ; 6,  $\nabla$ ; and 3,  $\square$ . Continuous lines are equilibrium calculations.



**Figure 5.** Comparison of experimental gas composition and thermodynamic equilibrium calculations. Sunflower oil reformed at a steam-to-carbon ratio S/C = 9. (H<sub>2</sub>  $\circ$ , CO<sub>2</sub>  $\square$ , CO  $\nabla$ , CH<sub>4</sub>  $\diamond$ ; continuous lines are equilibrium calculations).

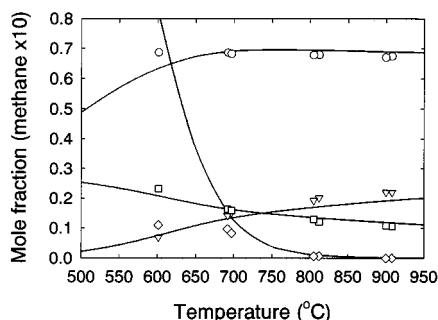


**Figure 6.** Comparison of experimental gas composition and thermodynamic equilibrium calculations. Sunflower oil reformed at a steam-to-carbon ratio S/C = 6. (H<sub>2</sub>  $\circ$ , CO<sub>2</sub>  $\square$ , CO  $\nabla$ , CH<sub>4</sub>  $\diamond$ ; continuous lines are equilibrium calculations).

yield in the zone from 650 to 850 °C at these S/C ratios, which is the temperature interval of interest for industrial steam-reforming units. For a S/C ratio of 3, a maximum yield of around 75% of the potential may be expected around 750 °C.

Figures 4–6 plot experimental and equilibrium gas compositions for each steam-to-carbon ratio versus the temperature at the exit of the catalyst bed (TI 04). The temperature does not substantially affect the hydrogen mole fraction at equilibrium, but it has a significant effect on the distribution of carbon among CO, CO<sub>2</sub>, and CH<sub>4</sub>. Essentially, higher temperatures tend to decrease the equilibrium concentrations of methane and carbon dioxide but increase the concentration of carbon monoxide. In this case, the hydrogen released by the disappearance of methane is consumed for transforming CO<sub>2</sub> into CO, and the hydrogen concentration is left almost constant. A higher steam-to-carbon ratio shifts the equilibrium toward higher concentrations of hydro-





**Figure 7.** Comparison of experimental gas composition and thermodynamic equilibrium calculations. Sunflower oil reformed at a steam-to-carbon ratio  $S/C = 3$ . ( $H_2$ ,  $\circ$ ;  $CO_2$ ,  $\square$ ;  $CO$ ,  $\nabla$ ;  $CH_4$ ,  $\diamond$ ; continuous lines are equilibrium calculations).

gen and carbon dioxide and lower concentrations of carbon monoxide and methane, although the effect of temperature is qualitatively the same at the three steam-to-carbon ratios we tested.

## Conclusions

Hydrogen can be produced from sunflower oil by catalytic steam reforming using commercial nickel-based catalysts and process conditions close to those for steam reforming of naphtha. Hydrogen yields from 72% to 87% of stoichiometric yield were obtained, depending on the steam-to-carbon ratio and the temperature of the catalyst at the exit of the steam-reforming reactor, both of which governed the equilibrium among gas species. Further conversion of carbon monoxide in downstream shift reactors would render hydrogen yields close to the maximum stoichiometric potential.

Thermal cracking of the vegetable oil competes with steam reforming, especially at gas temperatures above 650 °C. Extensive cracking of the oil will lead to the formation of aromatics and carbon-forming precursors that may deactivate the catalyst by carbon deposition. Consequently, the mixture of vegetable oil and steam should not be heated excessively before a substantial fraction of the oil has been converted by steam reforming. A steam-to-carbon ratio between 3 and 6 and a catalyst temperature above 600 °C at the entrance of the catalyst bed are suitable for hydrogen production. From the gas composition it may be concluded that catalyst exit temperatures of 750–800 °C will be required for a low concentration of methane in the product gas. Gasification of the carbon deposits by steaming at 850 °C appears to be an efficient way for recovering catalyst activity.

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