

Hydrogen production from used lubricating oils

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Abstract

Used lubricating oils (lube oils) are generated throughout the year and collected in central locations in many communities. Disposing lube oil in an improper manner contaminates environment to a great degree. Used lube oil can be valuable as a re-refined lubricant or as an energy source. Lube oil is a complex mixture of aliphatic and polycyclic hydrocarbons formulated to withstand high service temperatures in internal combustion engines. Both synthetic and mineral oils contain a high concentration of hydrogen (about 13–14 wt%). At the Florida Solar Energy Center, we have developed a process that converts lube oils to hydrogen and other valuable low molecular weight hydrocarbons. The lube oil reformation experiments were carried out using several commercially available dehydrogenation catalysts at a range of reactor temperatures and pressures, residence times and steam to carbon ratios. In this paper, the data obtained to date and the results are presented and discussed.

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1. Introduction

It is expected that near-term hydrogen (H_2) production in the emerging “hydrogen economy” will include cost-effective and clean processes that utilize local feedstocks. In that regard, used lubricating oils present a valuable, readily available and cost-effective resource for production of hydrogen. The amount of used lubricating oil available for hydrogen production is considerable (e.g. 45 million gallons per year in Florida alone). Used oil is available through out the year without any seasonal fluctuations at a relatively low cost (typically 10 cents/gallon delivered, in Florida). There are number of re-refining methods to clean the used lubricating oil and reuse it. Even the most advanced lubricant re-refining technology recovers only a portion of the used lube oil available. Re-refining plants employ energy intensive processes such as vacuum flashes, solvent extractions, distillation, demetallization, etc. and produce considerable amount of waste sludge that requires disposal. Thermochemical reformation of used lubricating oils for the production of hydrogen presents a method for the waste volume reduction and facilitates waste disposal.

2. Background

Used lubricating oil is a very complex mixture of low and high (C_{15} – C_{50}) molecular weight aliphatic and aromatic hydrocarbons [1,2], additives, metals, and various organic and inorganic compounds. The chemical composition of used lubricating oil varies widely and depends on the original crude oil, the processes used during refining, the efficiency and type of engine that utilized the oil, products of gasoline or diesel combustion, the additives added to the fuel and to the original oil, and the length of time that the oil remains in the engine. Used lubricating oil has a density (at 20 °C) of about 0.88 kg L^{-1} . Lube oils are designed to withstand very high service temperatures in the internal combustion engines and resist thermal degradation. Here, we report results for several processes for the reformation of used lubricating oils including supercritical water reformation, steam reformation and pyrolysis for the production of H_2 and other valuable low molecular weight hydrocarbons.

Elemental analysis of a sample of used lubricating oil obtained in Florida indicated 13.70 wt% hydrogen (See Table 1) content. This is twice hydrogen available from woody biomass and about three weight percent higher than that of vegetable oils. The high hydrogen content in the used lubricating oil makes it a valuable feedstock for hydrogen production.

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Table 1
Elemental analysis of Mobil One™ synthetic oil and a sample of used lubricating oil acquired in Florida

Elements (wt%)	Lube oil (synthetic)	Lube oil (used)
Hydrogen	13.37	13.70
Carbon	84.35	84.63
Oxygen	2.51	2.17
Sulfur	0.22	0.28
Nitrogen	<0.5	<0.5
H/C (mol/mol)	1.90	1.95

3. Experimental

A schematic diagram of the hydrogen production system for steam reformation of used lubricating oils is shown in Fig. 1. It includes: the feed and preheat section, a thermocatalytic reactor, product separation section, and a section to conduct product analysis.

In the feed and preheat section, lube oil and water are compressed using two HPLC pumps that deliver a maximum flow rate of 100 mL/min. Water is preheated to a desired temperature using ceramic heaters and mixed with the lube oil. Then, the mixture enters into the thermocatalytic reactor. The reaction zone is within a tubular reactor constructed from Inconel alloy 600 (for low temperature, high pressure service)

and Hastalloy 800T (for high temperature, low pressure service). The volume of catalyst bed within the reactor is adjusted by varying the packing length of the catalyst which allows the residence times within the catalyst bed to be varied. Reactor pressures and temperatures were monitored, in real time, at the reactor inlet and outlet, and within the catalyst bed.

In the posterior section, a series of in line filters trap any char that may be produced in the reactor. Following the product separation stage, the high pressure liquid/gas mixture enters a backpressure regulator, which lowers the pressure down to near atmospheric. A condenser is located after the backpressure regulator for separating the liquid and gaseous phases. The exit gas splits into two streams. A very small stream passes into a gas chromatograph equipped with thermal conductivity and flame ionization detectors and analyzed for hydrogen, carbon dioxide, carbon monoxide, methane, ethane, ethylene, hexane, pentane and benzene, among others. The remaining portion passes through a volumetric bubble flow meter and vented out. The liquid portion is collected at the bottom of the condenser and sampled for analysis periodically.

For the safety sake, the reactor was shielded and several pressure relief valves were installed at strategic locations in the process lines. We used corrosion resistant stainless steel 316 tubing, interconnects and fittings throughout.

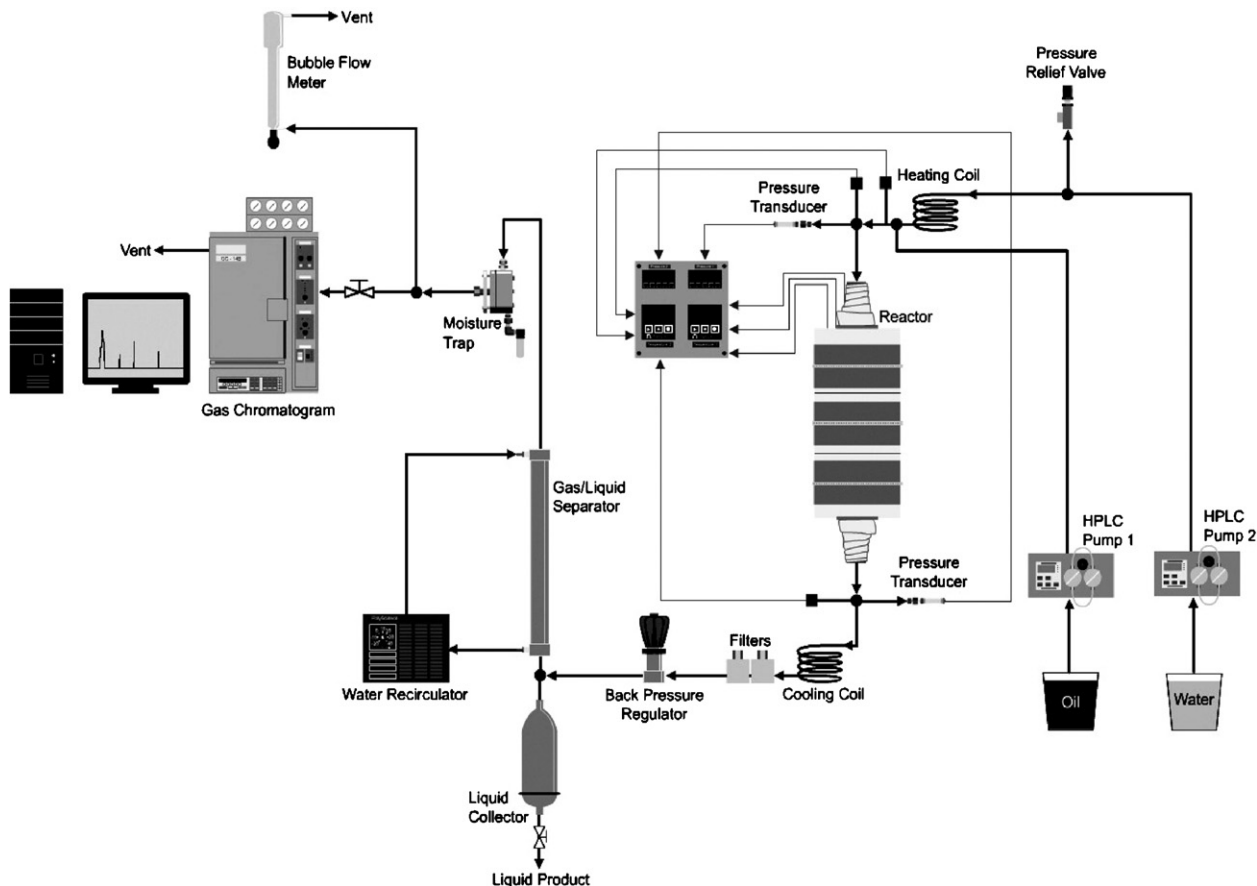


Fig. 1. Schematic diagram depicting experimental setup for the thermocatalytic reformation of used lubricating oil.

4. Results and discussion

4.1. Supercritical water reformation of lube oils

The use of supercritical water has several advantages over atmospheric steam. Supercritical fluid is one that is heated above its critical temperature (T_c), and compressed above its critical pressure (P_c). Water becomes a supercritical fluid at temperatures and pressures at or above 374.2 °C and 22.1 MPa, respectively. A key advantage of chemistry in supercritical water is that it is possible to vary the properties of the reaction medium such as density, viscosity, and diffusivity by manipulating the pressure and temperature and optimizing the reaction medium without changing the solvent (water). Furthermore, the ion product, or dissociation constant (K_w) for water near the critical point, is about 3 orders of magnitude higher than that of ambient liquid water. Thus, under certain conditions, near-critical and supercritical water can possess a higher H^+ and OH^- ion concentration than liquid water making dense high temperature water an effective medium for acid- and base catalyzed reactions of organic compounds [3]. However, beyond the critical point, K_w falls precipitously—making it a poor medium for ionic chemistry. According to Antal et al., free-radical mechanisms are favored when the dissociation constant $K_w \ll 10^{-14}$ (mol kg^{-1})² while ionic mechanisms prevail at $K_w > 10^{-14}$ (mol kg^{-1})² [4]. Under our experimental conditions (450 °C and 22.06 MPa corresponding to a water density of about 0.1 g cm⁻³), the dissociation constant, calculated using a correlation given by Marshall and Franck [5], was found to be about $K_w = 10^{-22.3}$ (mol kg^{-1})²—which is much less than 10^{-14} (mol kg^{-1})². So, it is expected that, under our experimental conditions, we find no ionic mechanisms present. This was found to be the case as discussed later in this section.

Another advantage of using supercritical water as a reaction medium for hydrogen production from used oils is that very little energy is required to pressurize water and oil to 22.1 MPa while, the gaseous products including hydrogen are produced already pressurized at high reactor pressure. This will drastically reduce purification and storage costs since most of the energy spent to liquefy hydrogen is for its compression.

A series of steam reforming experiments were carried out at water temperature of 450 °C and 22.06 MPa pressure (corresponding to a water density of about 0.1 g cm⁻³) using a commercially available sample of virgin synthetic lubricating oil (Mobil One™). We employed nickel [6] and carbon based catalysts as well as an alkali (KOH) catalyst in all of the supercritical water reformation tests. Experiments were conducted for five continuous hours at above supercritical water conditions and the product gas was sampled and analyzed in one hour intervals. Water to oil ratio of four to one was used for all the reforming experiments reported here.

The following observations were made from the results: (1) reformation runs using nickel catalysts yielded higher rate of gas production than the uncatalyzed reaction in the first hour of the run, (2) after 5 h of continuous operation, the Ni catalysts were completely deactivated and no longer demonstrated

catalytic activity, and (3) the rate of gas production from uncatalyzed runs did not change during the 5-h operation. Analysis of the exit stream indicated that hydrogen and carbon dioxide were the main reaction products with carbon monoxide, methane, ethane and ethylene present in very small quantities.

Fig. 2 gives the comparative results depicting the rate of gas production from the supercritical water reformation of virgin Mobil One™ synthetic lube oil in the presence of various dehydrogenation catalysts examined. It can be seen that the nickel catalysts rapidly deactivate in the supercritical water reaction condition. Another observation was that even though the rate of gas production dropped as a function of time, the reaction selectivity toward hydrogen and CO₂ remained unchanged throughout the entire 5-h period. In other words, catalyst deactivation lowers the conversion but does not significantly affect the selectivity of the process toward hydrogen and CO₂ formation.

In the heterogeneous catalytic processes described above, coking does occur and blocks the active sites on the catalyst surface—reducing hydrogen production yield. We carried out several experiments using a homogeneous catalyst, potassium hydroxide. The rationale for using a homogeneous catalyst is that all the reactants as well as the catalyst are in a single phase and as such the catalyst should remain active. In addition, homogeneous catalysis has been shown to yield better selectivity and allow easier process modification and optimization.

Kruse et al. have shown that alkali salts such as potassium hydroxide (KOH) and potassium carbonate (K₂CO₃) promote gasification of a biomass model compound (pyrocatechol) in supercritical water at temperatures as low as 500 °C [7]. According to Kruse et al., addition of alkali metal hydroxides increases the yield of hydrogen and carbon dioxide formation and reduces the yield of carbon monoxide and char formation during the gasification of pyrocatechol in the supercritical water. In their study, KOH was dissolved in the feed water to the

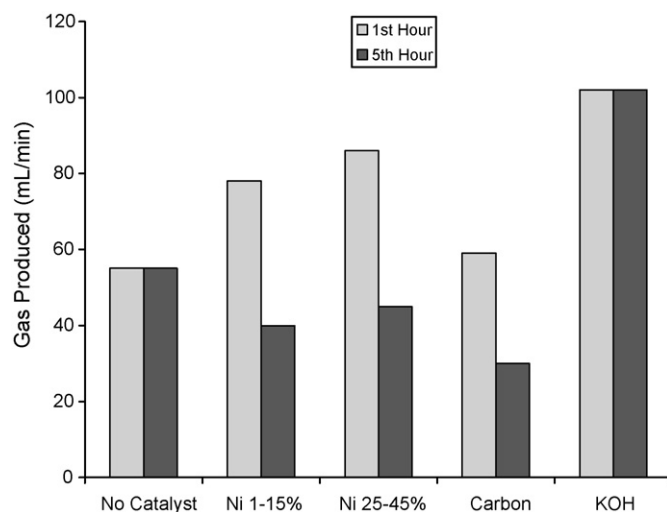


Fig. 2. Comparison of alkali catalyst with the carbon and Ni based catalysts during supercritical water reformation of virgin Mobil One™ synthetic lube oil (water temperature = 450 °C and pressure = 22.06 MPa corresponding to a water density of about 0.1 g cm⁻³).

reactor, which acted as a catalyst for the reformation reaction in the supercritical water. Addition of alkali metal hydroxides led to the formation of formates, which subsequently decomposed to form hydrogen and carbon dioxide. Formic acid appears to be an intermediate product of the water-gas shift reaction.



Also, Watanabe et al. have demonstrated that sodium hydroxide (NaOH) is an effective catalyst for the gasification of glucose and cellulose in low temperature (673 K) supercritical water [8]. Unlike biomass model compounds, hydrocarbons are known to be difficult to gasify in supercritical water [9]. According to Watanabe et al., partial oxidation of linear chain and aromatic hydrocarbons in high density (more than 0.25 g/cm³) and low temperature (400 °C) supercritical water generates H₂ and CO, selectively—but, the yield of hydrogen is low (less than 2% of the hydrogen in feedstock) [10]. More recently, Watanabe et al. have studied the catalytic (ZrO₂ and NaOH) partial oxidation of *n*-hexadecane employing a batch type reactor in supercritical water at 400 °C, water density of 0.52 g/cm³ (40 MPa pressure), and an O/C ratio of 0.3. The use of these catalysts did not increase *n*-hexadecane conversion but did promote formation of 1-alkenes and hydrogen [11].

In this study, we performed several experiments at near-critical water conditions to determine the effect of KOH addition on the lube oil reformation. Typical results are given in Fig. 2 that compares the rate of gas production from the KOH catalyzed reformation of lube oil in supercritical water to that of several commercially available heterogeneous catalysts described before. Amount of gas produced in the presence of KOH catalyst at 1 and 5 h through the runs were, respectively, 15 and 55% higher than those obtained from the Ni and carbon based catalysts. Even though the use of KOH as a catalyst for the reformation of virgin Mobil OneTM lube oil increased the rate of total gas generated (with no noticeable degradation of the catalyst activity), the hydrogen yields were still low.

The role(s) of the water in the hydrothermal reactions (above 200 °C and supercritical water) are important to the reaction chemistry and kinetics. A comprehensive review of the roles of water for chemical reactions in high temperature water is given by Akiya and Savage [12]. In general, reactions in supercritical water are a combination of hydrolytic and pyrolytic reactions, with the pyrolysis pathway dominating as temperature is increased and the hydrolysis pathway dominating as water density is increased. Furthermore, it is known that for a reactant molecule to be hydrolyzed, it must have a heteroatom bonded to a saturated carbon atom. Molecules with carbon–carbon bonds alone do not show the product slate typical of hydrolysis [13]. In summary, hydrothermolysis of lube oil in near-critical water at a density of 0.1 g/cm³, where the pyrolytic path dominates, results in a relatively low conversion with free-radical chemistry being the primary pathway. Water does not appear to be either a reactant (i.e. a means of incorporating oxygen functionalities into the lube oil) or a catalyst.

In order to increase the yield of gaseous products, in general, and hydrogen, in particular, we opted to lower the reaction

Table 2

Rate of gas production from reformation of lube oil at various feed water and lube oil flow rates at reformer temperature of 715 °C and 1 atm

Input synthetic oil ^a (mL/min)	Feed water (mL/min)	Gas produced (mL/min)
0.5	1	255
1	0.5	524
1	1	498
1	2	466
1	3	452

^a Virgin Mobil OneTM oil.

pressure and increase the reaction temperature. A brief discussion of the results obtained from the low pressure, higher temperature steam reformation and thermal cracking of lubricating oils is given below.

4.2. Steam reformation of lube oils

Table 2 depicts the rate of gas produced from steam reformation of virgin Mobil OneTM oil for a range of oil to water feed ratios at 715 °C and 1 atm. The steam to oil ratio of 1 to 0.5 produced as much as 14% more gas than runs with other water to oil feed ratios. Table 3 gives the process conditions and results for all the steam reformation experiments. For the virgin synthetic (Mobile OneTM) oil, with the steam to oil feed ratio of 2 to 1, an increase in the reformation temperature from 715 to 850 °C increased the gas yield by 11%. For the used oil, increasing the temperature from 750 to 850 °C increased the gas yield by 20%.

The results indicate that a reformation temperature in the range of 850 °C (at 1 atm) favors high gas yields. Temperature above this point increases the yield of char production with minimal effect on the conversion efficiency. In some cases, the production of char in the reactor lines was excessive resulting in the experiment to halt.

Figs. 3 and 4 depict the product gas composition from virgin synthetic (Mobile OneTM) and used lube oil steam reformation experiment. The result shows that the predominant gases produced were hydrogen, methane, ethylene, ethane acetylene and very low concentrations of carbon monoxide and carbon dioxide.

Results from the experiment 3, 4, 5, 9, and 12 (See Table 3) imply that, high temperature reformation of lube oil using KOH catalyst doesn't increase total gas yield and has no significant effect on the selectivity toward hydrogen production. As discussed in section 4.1, addition of alkali metal hydroxides leads to the formation of formates from CO and water, which subsequently decompose to form H₂ and carbon dioxide. Since very little or no CO was produced in the high temperature steam reformation process, it is clear that KOH does not play a role as catalyst toward increasing the yield of gas generated.

Table 4 gives the total amount of hydrogen produced at different reformer temperatures and 1 atm with and without input water. For the same temperature and pressure, the volume and composition of the gas produced were basically same for the experiments with and without feed water to the reformer.

Table 3

Volume and composition of gas produced by the steam reformation of virgin synthetic (Mobil One™) and used lube oils at 1 atm for various reformer temperatures and oil to water feed ratio of 2:1, with and without KOH added

Exp. no.	Catalyst	Temperature (°C)	Total volume of gas produced per mL of oil fed (mL)	Composition of product gas, mL of total								Mass of hydrogen in the product gas/ mass of hydrogen in the feed oil	Gas yield wt%
				H ₂	CO	CH ₄	CO ₂	C ₂ H ₂	C ₂ H ₆	C ₂ H ₄	>C ₃		
1 ^a	None	715	448	58	4.5	157	13.5	4.5	148	45	18	0.5761	26.54
2 ^a	None	750	461.5	69	5	157	14	–	157	46	14	0.5921	27.03
3 ^a	0.025 M KOH	750	466	60	3	136	6	2	183	30	47	0.5600	26.11
4 ^a	0.05 M KOH	750	482.5	67	3	170	4	2	180	34	22	0.6195	27.75
5 ^a	0.1 M KOH	750	488	81	3	167	4	2	167	44	31	0.6269	27.37
6 ^a	None	800	488	97.6	2.9	200	2.5	1	135.6	24.4	23.9	0.6028	24.64
7 ^a	None	850	504	124.6	5	194.5	3.5	3	118.9	11	43	0.5613	22.25
8	None	750	383	50	4	149	–	–	103	31	46	0.4601	19.41
9	0.1 M KOH	750	363.5	62	4	105	7	11	116	15	44	0.4065	19.13
10	None	800	428.5	72.9	4.3	162.8	– ^b	–	111.4	21.4	55.7	0.4891	20.38
11	None	850	480	91.2	4.8	196.8	–	–	120	19.2	48	0.5594	22.59
12	0.1 M KOH	850	218	64	4	63	11	2	41	4	28	0.1318	9.34
13	None	880	500	110	5	195	–	–	105	15	70	0.5391	20.96

^a Virgin Mobil One™ synthetic oil.

^b Insignificant.

Our results imply that addition of feed water during high temperature reformation of lube oil had no appreciable effect on the yield of hydrogen or the amount of gas produced. It appears that, under our experimental conditions, water acts as a heat transfer fluid rather than a reactant. Thus, addition of water does not appear to contribute to the amount of hydrogen generated during the reformation process. Reducing the amount of feed water added to the input stream should lower the amount of disposable waste generated from reformation of lube oil and also reduce the process heat duty. These results led us to conduct several experiments involving direct thermolysis of lube oils in the absence of added water.

4.3. Thermolytic cracking of lube oils

Table 5 depicts the volume and composition of gas produced from direct thermolytic (no catalyst) cracking of virgin

synthetic (Mobil One™) and used lube oils at various temperatures and 1 atm. For the virgin synthetic oil (Mobile One™), increasing the reactor temperature from 750 °C to 850 °C results in 8% increase in the yield of gas produced. For the used oil, increasing the temperature from 750 to 850 °C increases the gas yield by about 29%. Temperatures above 880 °C increase the yield of char production with minimal effect on the amount of gas produced per unit weight (or volume) of oil fed into the reformer. In some cases (high temperatures), the extent of char production was so high that resulted in the process lines becoming completely clogged within a short period of time. We made similar observation at high temperatures during steam reformation experiment described before.

Results obtained from the direct thermolytic reformation of the virgin synthetic (Mobile One™) oil indicate that 58–65% of the total mass of hydrogen in the oil fed into the reformer was

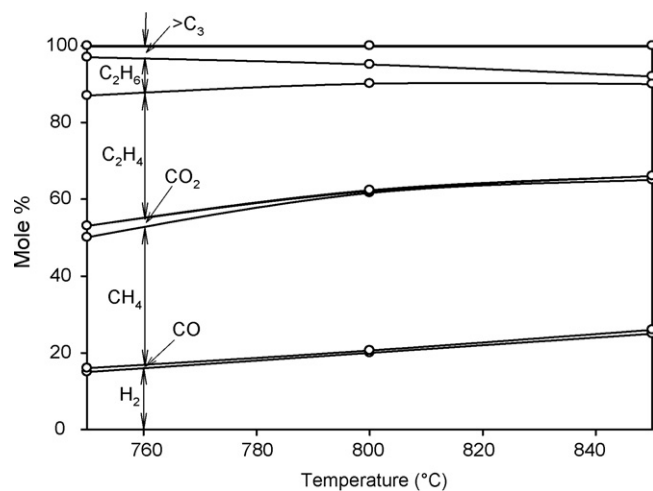


Fig. 3. Stacked presentation of the product gas slate from the steam reformation of virgin synthetic lube oil (Mobil One™); data: open circles, solid lines: spline fit to data points.

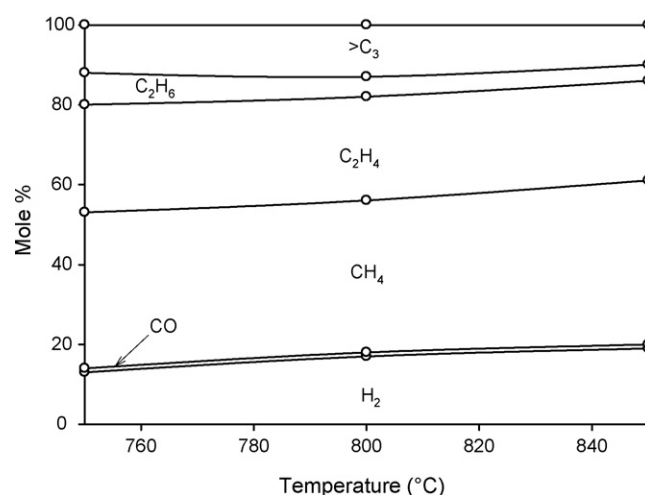


Fig. 4. Stacked presentation of the product gas slate from the steam reformation of used lube oil; data: open circles, solid lines: spline fit to data points.

Table 4

Total mass of hydrogen produced in 1 h for various reformer input and operating conditions at 1 atm

Lube oil ^a to water feed ratio (mL/min)/ (mL/min)	Temperature (°C)	Total amount of hydrogen in the feed (g)	Amount of hydrogen in the product gas (g)	Total volume of gas produced (L)	Volumetric rate of liquid product collected (mL/min)
2/1	750	20.46	8.17 (4.1)	55.44 (27.72)	1.66
3/0	750	20.40	12.46 (4.2)	82.8 (27.6)	1.07
2/1	800	20.46	8.32 (4.2)	58.56 (29.28)	1.64
3/0	800	20.40	13.35 (4.5)	89.7 (29.9)	1.05
2/1	850	20.46	7.74 (3.9)	60.48 (30.24)	1.68
3/0	850	20.40	12.02 (4.0)	90 (30)	1.20

() Total volume of product gas produced per 1 mL of lube oil fed into the reformer.

^a Virgin Mobil One™.

Table 5

Volume and composition of gas produced from the thermolytic (no catalyst) reformation of virgin synthetic (Mobil One™) and used lube oils at various temperatures and 1 atm

Exp. no.	Temperature (°C)	Total volume of gas produced per mL of oil fed (mL)	Composition of product gas, mL of total								Mass of H ₂ in the product gas/mass of H ₂ in the feed oil	Total gas yield wt%
			H ₂	CO	CH ₄	CO ₂	C ₂ H ₂	C ₂ H ₆	C ₂ H ₄	>C ₃		
14 ^a	750	460	56	2	176	2	1	146	49	28	0.6108	41.2
15 ^a	800	498.3	91.2	2.5	223.2	2.5	1	127	38.4	12.5	0.6544	41.1
16 ^a	850	500	115	2	220	2	6	102	16	37	0.5891	35.51
17	800	354	60.2	3.5	148.8	– ^b	3.54	92.1	24.8	21.3	0.4401	28.11
18	850	500	105	5	230	–	–	115	25	20	0.6225	37.96
19	880	500	150	5	230	–	–	70	50	30	0.5705	31.23

^a Virgin Mobil One™ synthetic oil.^b Insignificant.

converted to hydrogen in the output gas. Likewise, results obtained from the direct thermolysis of the used lube oil show that 40–63% of the total mass of hydrogen in the used oil fed into the reformer was converted to hydrogen in the output gas. Recycling the unconverted liquid at the exit with the fresh feed into the reactor has potential to increase the yield of the gaseous products from the reformer.

Figs. 5 and 6 depict the product gas slate from thermolytic cracking of the virgin synthetic (Mobile One™) and used lube

oil. The composition of the product gas generated by the thermolytic decomposition of these oils was very close to that obtained from the steam reformation experiments. The main gaseous species generated were H₂, CH₄ and ethylene at 17–30%, 40–45% and 15–25%, respectively. Very small amounts of CO and CO₂ were also generated (0.5–1%). It can be seen that the amount of CO and CO₂ produced by the thermal cracking of lube oils are much less than that normally obtained by conventional steam reformation of methane or hydro-

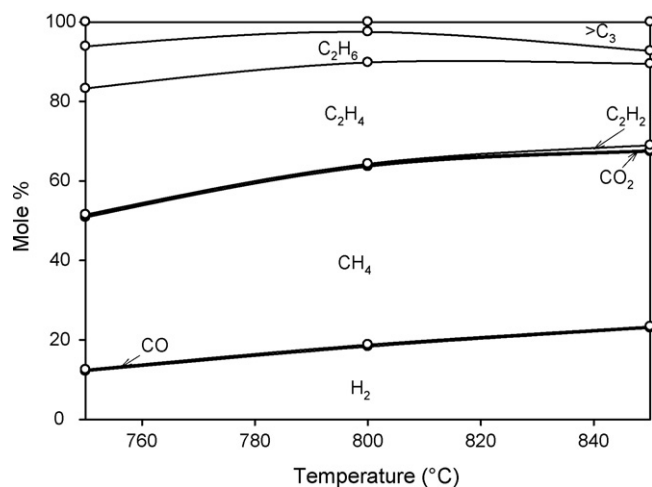


Fig. 5. Stacked presentation of the product gas slate from the thermal cracking of virgin synthetic lube oil (Mobil One™); data: open circles, solid lines: spline fit to data points.

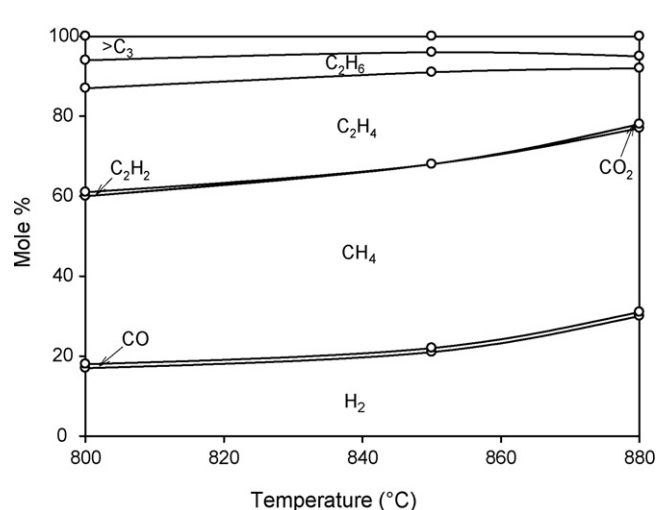


Fig. 6. Stacked presentation of the product gas slate from the thermal cracking of used lube oil; data: open circles, solid lines: spline fit to data points.

carbons. As noted before, presence of water does not appear to affect, chemically, thermolysis of lube oils and only acts as a heat transfer medium.

Gases species other than H_2 that are produced during pyrolysis of lube oils are low molecular weight hydrocarbons such as CH_4 , C_2H_6 , C_2H_4 and C_2H_2 . These hydrocarbon gases can be reformed easily at the posterior of the cracking reactor to generate additional hydrogen or extracted for use as chemical feedstocks.

5. Conclusions

Hydrogen production from used lube oil via thermal cracking can be attractive process both environmentally and economically. We have demonstrated the feasibility of hydrogen production via thermal cracking of lubricating oils—both virgin synthetic oil (Mobile OneTM) and a sample of used lube oil obtained in Florida.

Performance of several dehydrogenation catalysts such as nickel, carbon, and an alkali based catalyst for reformation of lube oils and production of hydrogen was investigated. Both nickel and carbon based catalysts performed poorly toward hydrogen production during steam reformation of lube oils—due to deactivation. The amounts of gas produced using KOH catalyst were higher than those obtained from the Ni and carbon based catalysts. Utilizing KOH as a catalyst for the reformation of lube oils increased the total yield of all the gaseous species produced (with no noticeable degradation of the catalyst activity) with high selectivity toward hydrogen. However, the hydrogen yields were low. In order to increase the yield of gaseous products and particularly that of hydrogen, it was necessary to lower the reaction pressure and increase the reaction temperature.

Total gas produced and the yield of hydrogen were significantly higher during both steam reformation and direct thermal cracking of the lube oils at 1 atm and reformer temperatures above 715 °C as compared with those obtained by supercritical water reformation (65% of hydrogen contained in oil, compared with only about 5% from supercritical water reformation). The high temperature, low pressure process also yielded lower concentrations of CO_2 and CO in the output gas (30% compared with only 1% by volume of gas produced by supercritical water reformation).

For the same temperature and pressure, the yield and composition of the gas produced by the steam reformation of lube oils were basically same regardless of whether or not the input stream to the reformer contained water. Results imply that addition of feed water during high temperature reformation of lube oil has no appreciable effect on the yield of hydrogen or the amount of gas produced. Under our experimental conditions,

water appears to act as a heat transfer fluid rather than a reactant. Thus, addition of water did not contribute to the amount of hydrogen generated during the reformation process. Results obtained from the direct thermolytic reformation of the virgin synthetic (Mobile OneTM) oil and used oil showed that, respectively, 58–65% and 40–63% of the total mass of hydrogen in the oil fed into the reformer was converted to H_2 in the output gas.

Composition of the gaseous species generated by thermal cracking and steam reformation of lube oils were basically the same and included mainly hydrogen, methane and ethylene at 17–30%, 40–45% and 15–25%, respectively. Under our experimental conditions, presence of water did not appear to affect, chemically, thermolysis of lube oils and only acted as a heat transfer medium. Direct thermolysis of lube oils requires less energy and produces about one third less disposable waste (compared with the steam reformation process).

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References

- [1] I.R. Kaplan, H.M. Shan-Tan Lu, J. Alimi, MacMurphey, *Environ. Forensics* 2 (2001) 231.
- [2] W.L. Bider, et al., Individual sample fuel mixture composition data, Prepared for EPA Office of Solid Waste and Energy Response, Document No. 530-SW-013.
- [3] P.E. Savage, *Chem. Rev.* 99 (1999) 603–621.
- [4] M.J. Antal Jr., A. Brittain, C. DeAlmeida, S. Ramayya, J.C. Roy, *Supercritical fluids*, in: T.G. Squires, M.E. Paulaitis (Eds.), ACS Symposium Series 329, 1987, pp. 77–86.
- [5] W.L. Marshall, E.U. Franck, *J. Phys. Chem. Ref. Data* 10 (2) (1981) 295–304.
- [6] L. Garcia, R. French, S. Czernik, E. Chornet, *Appl. Catal. A: Gen.* 201 (2000) 225.
- [7] A. Kruse, D. Meier, P. Rimbrecht, M. Schacht, *Ind. Eng. Chem. Res.* 39 (2000) 4842.
- [8] M. Watanabe, H. Inomata, K. Arai, *Biomass Bioenergy* 22 (2002) 405.
- [9] T. Funazukuri, N. Wakao, J.M. Smith, *Fuel* 69 (1990) 349.
- [10] M. Watanabe, M. Mochiduki, S. Sawamoto, T. Adschiri, K. Arai, *J. Supercrit. Fluids* 20 (2001) 257.
- [11] M. Watanabe, H. Inomata, M. Osada, T. Sato, T. Adschiri, K. Arai, *Fuel* 82 (5) (2003) 545–552.
- [12] N. Akiya, P.E. Savage, *Chem. Rev.* 102 (2002) 2725–2750.
- [13] K.M. Benjamin, P.E. Savage, *J. Supercrit. Fluids* 31 (2004) 301–311.