Oxygenated Fischer-Tropsch Derived Diesel Fuel

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There is a growing need to provide clean and efficient diesel fuels in improved diesel engines to replace gasoline now used in trucks, sports utility vehicles (SUVs) and other means of transportation. The gain in efficiency will be large with subsequent smaller releases of global warming gases. These new fuels must have high cetane numbers and, importantly, must meet new emission standards, especially in the lowering of particulate matter emissions. Exhaust particulate emissions from diesel engines can be as much as ten times greater than those from gasoline engines. As a result, focus on reduction of particle matter emissions from diesel engines is an environmental problem of great concern.

It is known that, when an oxygenated fuel blend is combusted, it can effectively deliver oxygen to the pyrolysis zone of a burning fuel, resulting in reduced particle matter generation. Data indicate that particle matter emission reductions of 4-10% can be achieved for each 1% of oxygen blended into diesel fuel by incorporation of certain oxygenated compounds, e.g, glycol ether. Southwest Research Institute (SwRI) blended 15 % of dimethyl acetal, which has 6% oxygen, into superclean diesel from petroleum; particle matter emissions went down by 40% by this addition. It is important to determine whether the kind of oxygen in the additive is important and whether oxygenates of different structures, added together, reinforce each other.

As proposed, we listed a number of oxygenated compounds that could be added to diesel fuel to lower particle matter emissions. However, Dr. Bill Piel of the Oxygenate Analysis Project has furnished us with a list of some forty oxygenated compounds that are currently being surveyed as candidates for addition to petroleum low sulfur diesel fuel.

We have therefore directed our efforts to obtain high cetane oxygenated diesel fuel in the other direction highlighted in our proposal, namely via the preparation of oxygenated diesel fuel via the Fischer-Tropsch reaction. This approach does not use added oxygenated compounds that, while likely a viable direction, could have certain costs involving solubility, toxicity and other possible problems.

The Fischer-Tropsch (F-T) reaction converts synthesis gas, composed of various proportions of carbon monoxide and hydrogen, to straight-chain paraffins (alkanes) with cobalt catalysts and to a mixture of straight-chain paraffins and olefins with iron catalysts. The Shell F-T plant in Malaysia, with a cobalt catalyst, used the F-T process to produce diesel fuel with a cetane number of about 70; the fuel contained no aromatics and no sulfur. The state of California has imported some of this F-T diesel fuel from Shell and added small amounts to petroleum-derived diesel fuels to meet their diesel fuel environmental standards.

Our project aims to convert synthesis gas to F-T products from which environmentally clean diesel fuels containing 4-10 wt% oxygen in the hydrocarbon chain can be produced. The F-T diesel fuel has a high cetane number, which would probably be reduced to about 60 by the addition of oxygen atoms in the chain. It is soluble in petroleum-derived diesel fuel and should be effective in reducing particle matter emissions. The F-T product, as has been done in California, would be used an additive to diesel from petroleum to help reduce emissions and raise cetane number.

For this purpose, a fixed bed continuous F-T unit has been constructed and is now operational. F-T products, from gases to waxes, have been produced using a cobalt catalyst. Present work is centered on a system for analysis of the complex mixture of products; this should be completed in the next two months. The F-T unit is an automatic high-pressure fixed bed reaction system. A computer is used to control the oven temperature, mass flow meters and sampling valves. Temperatures, flow rates and sampling times are also recorded by computer. Three GC columns are equipped to analyze the complex products of the F-T reaction. A HP Chemstation is used to control the GCs and analyze the collected data. A Visual Basic program was written to integrate the FC data and calculate the conversions and product distributions. A GC-MS is used to identify the components in products of the F-T synthesis.

A ruthenium-promoted Co/Al_2O_3 catalyst was prepared by incipient wetness impregnation. The support was γ-Al_2O_3 calcined at 500°C for 10 hours before impregnation. Cobalt nitrate and ruthenium nitrosyl nitrate were dissolved in de-ionized water and co-impregnated into γ-Al_2O_3 to form a catalyst with 20% Co and 0.5 wt% Ru. The catalyst was dried at 110°Cfor 12 hours and calcined in air at 300°C for 2 hours. $RuCo/Al_2O_3$ (0.2 to 2 g) was mixed with quartz sand and loaded into the reactor. The catalyst was reduced in pure H_2 at a rate of 50 ml/min, the temperature ramping from ambient to 350°C at 1°C, holding at 350°C for

10 hours. After reduction, the temperature was lowered to the reaction temperature. CO and H_2 flow rates were increased to a set value gradually in two hours while decreasing the argon (Ar) flow rate to avoid an initial temperature overshoot. Finally the Ar flow was maintained at 10 ml/min as a reference to calculate the CO conversion by

$$\text{Conversion} = [(C_{Ar})^{out}/(C_{Ar})^{in} - (C_{CO})^{in}/(C_{CO})^{in}]/[(C_{Ar})^{out}/(C_{Ar})^{in}]$$

F-T reactions were conducted at various temperatures and pressures. A good conversion of 36% was obtained at 220°C, 18 psi and 4.8 NL/hr.g. The activity remained constant during the run. The product is highly paraffinic. No wax product was collected at this reaction pressure. The conversion of CO and the average chain length of the product increased with increase in pressure. A substantial amount of wax was obtained at a pressure of 100 psig. Oxygenates were barely detectable in the F-T product on $RuCo/Al_2O_3$ at 220.

Oxygenates were obtained when the F-T reaction was conducted at lower temperatures. These oxygenates are mainly primary alcohols., identified by GC-MS. The alcohols ranged from C_6 to C_{19} as shown in Figure 1. At the initial stage of the reaction at 200°C and 100 psig, 3.2% of oxygenates were obtained in the collected oil product; the amount of oxygenates increased with time-on-stream. It increased to 6.2% after three days of reaction. Oxygenates could be further increased by lowering the temperature and raising the pressure of the F-T reaction. At 190°C and 200 psig, 10.2% of oxygenates were obtained in the collected oil product.

Product distributions of the collected oil fraction of the F-T product on $RuCo/Al_2O_3$ are shown in Figure 2. The amounts of oxygenates, olefins and paraffins are 10.2%, 26.5% and 63.3% respectively. The lower molecular weight products are rich in oxygenates and olefins; higher molecular weight products are more paraffinic.

Probe molecules containing oxygen, such as alcohols, ethers and unsaturated oxygen-containing molecules such as vinyl ethers are being added to the F-T reactions.

The goal is to incorporate oxygen atoms into the F-T products to reduce particulate matter emissions while maintaining high cetane numbers.
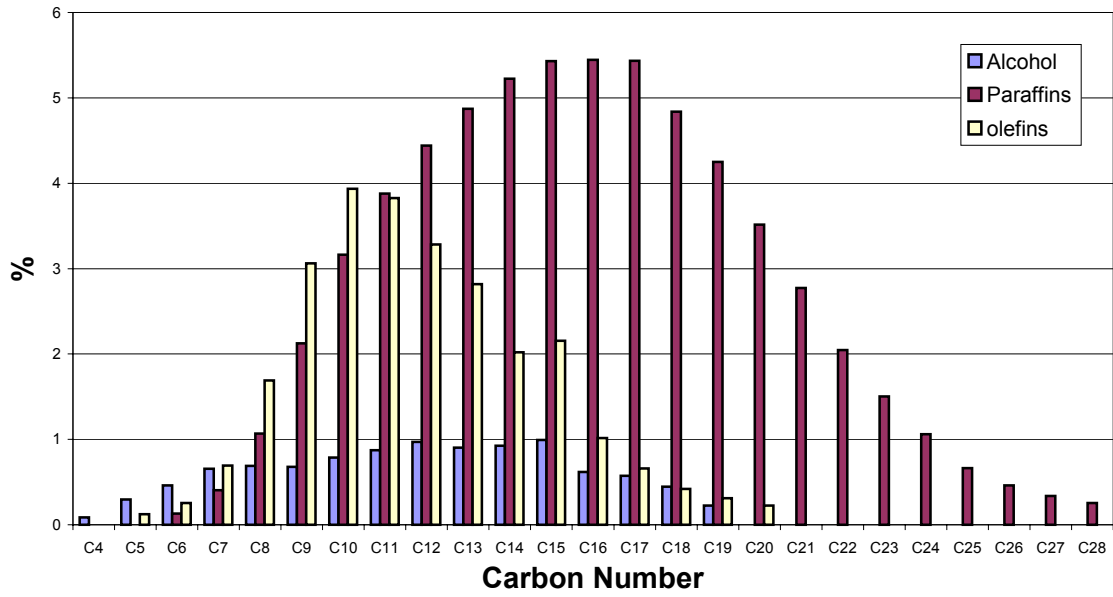
Figure 1. Product Distribution of Oil Fraction

Figure 2. Distribution of Alcohols.