FLOW REACTOR STUDIES OF SURROGATE BIODIESEL FUELS

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Background

There is a growing national trend toward incorporating renewable fuels as a means to reduce reliance on imported oil, promote production of domestic crops and decrease the production of green house gases. Soybean derived biodiesel fuel, in particular, has received significant attention in recent years because of its added benefit of reducing pollutant emissions from diesel exhaust.

The New Jersey Department of Transportation (NJDOT) is currently sponsoring a research study at Rowan University to evaluate the potential of biodiesel to reduce diesel emissions from mobile sources such as school buses and class 8 trucks. As part of the study, mobile school bus tests have recently been performed[1] with various biodiesel fuel blends (Fig.1). The results showed that HC, PM and CO emissions were significantly reduced for each of the biodiesel fuel blends tested (Fig. 2). Generally, however, the biodiesel blends resulted in slight increases in NO_x emissions.
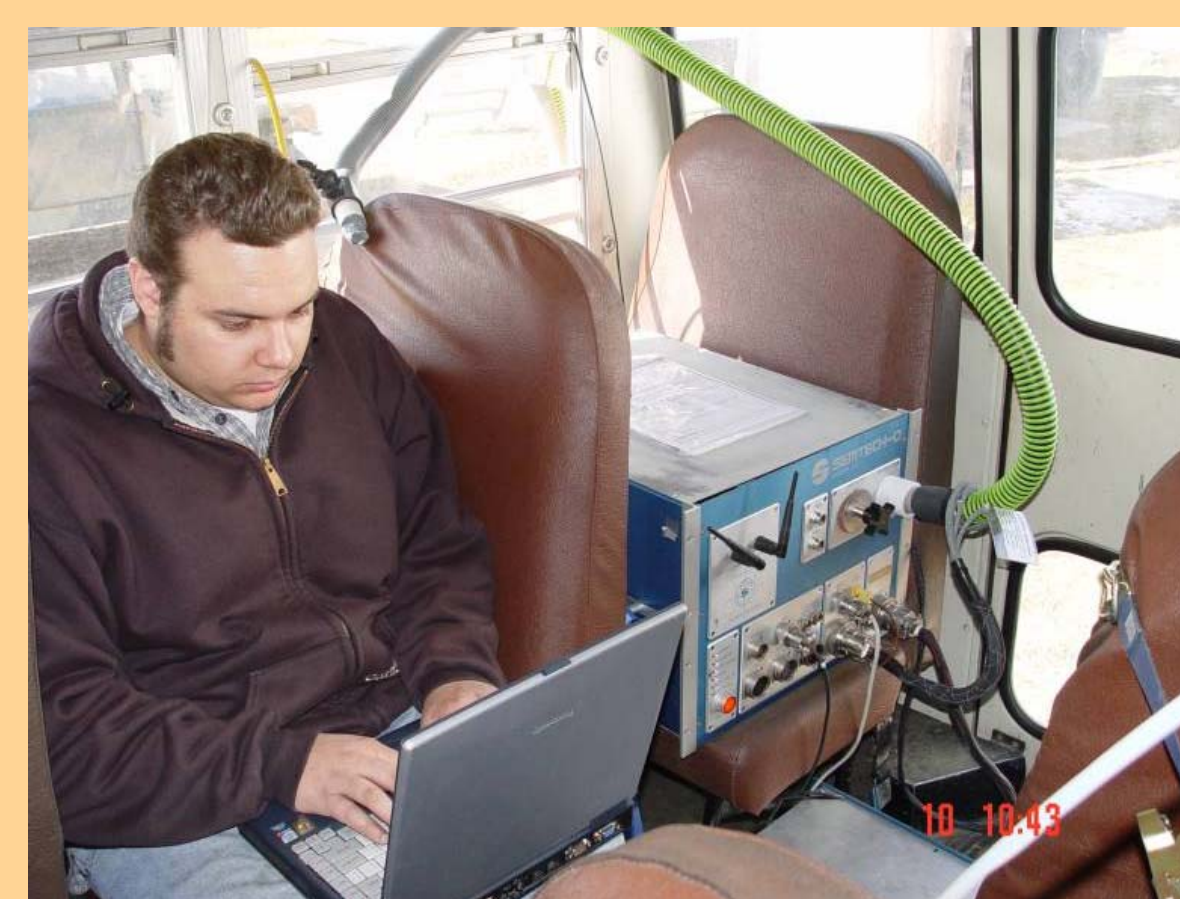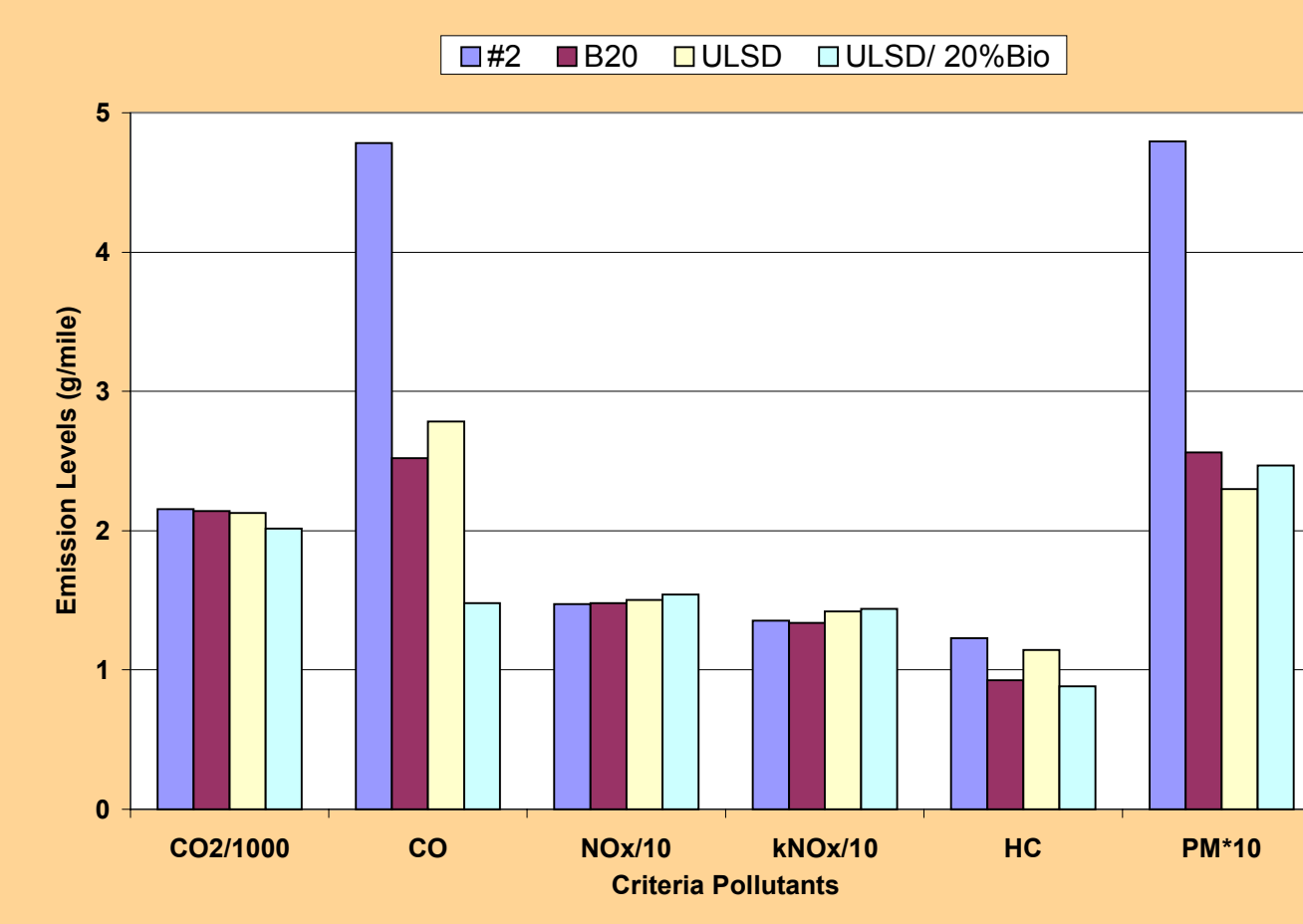

Figure 1. Mobile school bus emissions testing[1].

Figure 2. Exhaust emissions for T444E engine for four different fuels[1].

The results of the Rowan study agreed with those of a recent EPA study[2] which reported that neat soybean-derived biodiesel fuel results in a 47% reduction in PM, 48% reduction in CO and a 67% reduction in HC emissions in comparison with standard #2 petroleum diesel. However, the EPA report also showed that biodiesel fuels typically result in increased NO_x production and decreased fuel consumption.

Objective

A more fundamental understanding of the chemical kinetic mechanisms responsible for reduced HC, CO and PM emission (and increased NO_x) will ultimately result in more effective fuel blends that might produce reductions of all pollutants. Unfortunately, the chemical constituents of these oxygenated biodiesel fuels are quite complicated, consisting of mixtures of saturated and unsaturated methyl esters, containing carbon chains 15-20 or more atoms in length.

Since it has similar chemical features as the larger methyl esters found in biodiesel, Fisher and coworkers[3] have developed a detailed chemical kinetic mechanism (264 species, 1219 reversible reactions) of methyl butyrate. However, when the mechanism was developed, very little data existed for model testing and validation of the mechanism. Prior to the present study, the methyl butyrate mechanism had only been tested against a handful of low temperature, sub-atmospheric, closed vessel cool flame experiments which were performed in the 1950s. The objective of the present study is to perform flow reactor experiments to test the mechanism at conditions closer to those which occur within a compression ignition engine.

Experimental

This poster presents the results of new methyl butyrate flow reactor experiments performed using the Princeton Variable Pressure Flow Reactor (See Fig. 3). Reactivity experiments were performed at 12.5 Atm over a range of 500 to 900 K and equivalence ratio of 0.35 to 1.60.
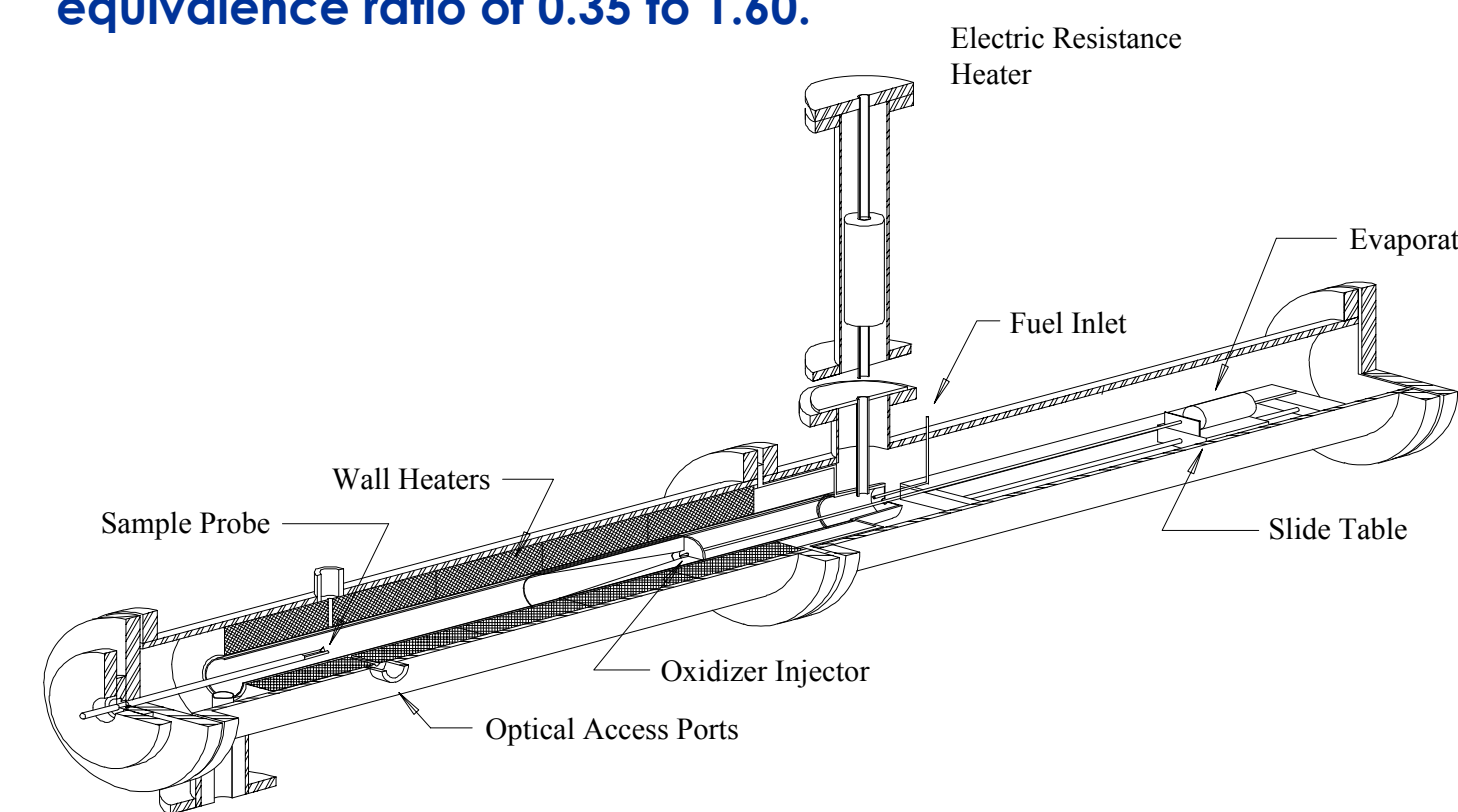

Figure 3. Princeton Variable Pressure Flow Reactor (VPFR).

Fisher Mechanism (Ref. 3)

Fisher and coworkers have developed a detailed chemical kinetic mechanism of methyl butyrate oxidation shown schematically in Figure 4.
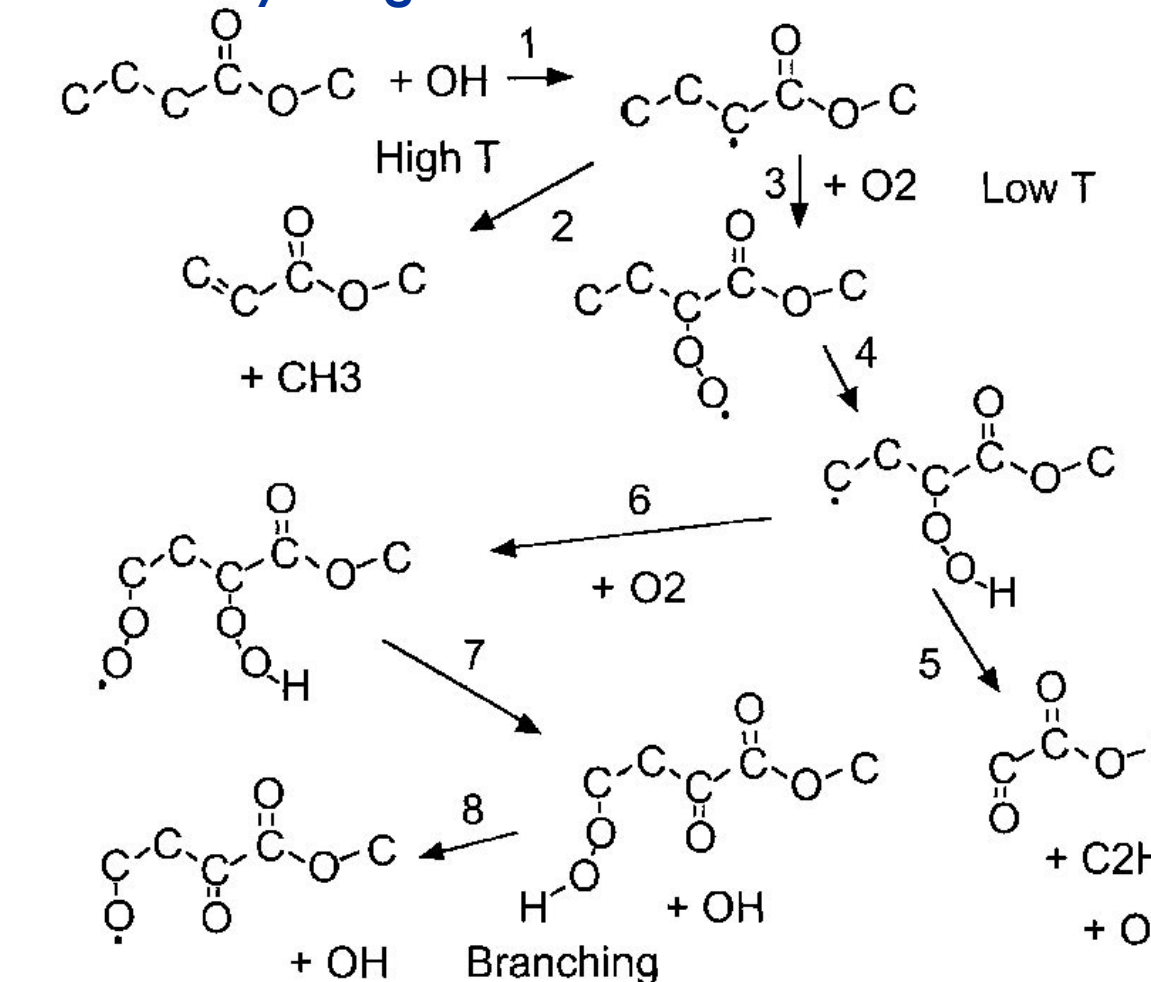

Figure 4. Schematic diagram of Fisher methyl butyrate kinetic mechanism (Reprinted from Ref. 3).

A Surrogate Fuel for Biodiesel

Biodiesel is broadly defined by the National Biodiesel Board as the mono alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, for use in compression-ignition engines[4]. Soybean oil, which is the most common feedstock for biodiesel used in the United States, contains predominantly unsaturated acids, with a high concentration Oleic and Linoleic acids as shown in Table 1.

Table 1. Typical soybean methyl ester constituents[4,5].

Acid Chain	Weight Percent	Molecular Weight	Chemical Formula
Palmitic	12.0	270.46	$CH_3(CH_2)_{14}CO_2CH_3$
Stearic	5.0	298.52	$CH_3(CH_2)_{16}CO_2CH_3$
Oleic	25.0	296.52	$CH_3(CH_2)_7CH=CH(CH_2)_7CO_2CH_3$
Linoleic	52.0	294.48	$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7CO_2CH_3$
Linolenic	6.0	292.46	$CH_3CH_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_7CO_2CH_3$

As a first step in understanding the chemical kinetics of these long-chain, oxygenated fuels it is necessary to identify surrogate fuels that contain features similar to the larger methyl esters found in biodiesel. Fisher and coworkers[3] have proposed methyl butyrate ($nC_3H_7C(=O)OCH_3$) and methyl formate $HC(=O)-OCH_3$ as surrogate fuels for biodiesel studies since they have similar chemical features as the larger methyl esters.
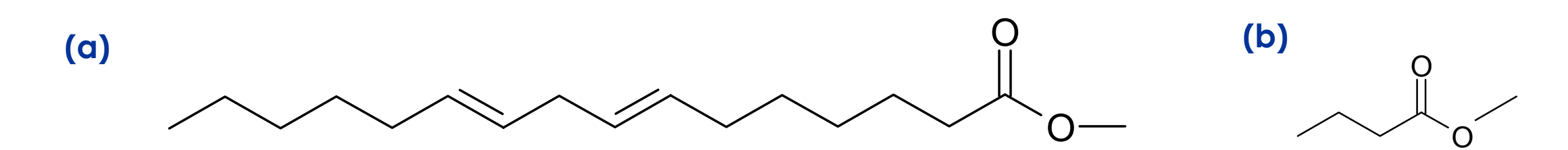

Figure 5. Chemical structure of (a) a soybean methyl ester biodiesel constituent and (b) the proposed surrogate fuel methyl butyrate.

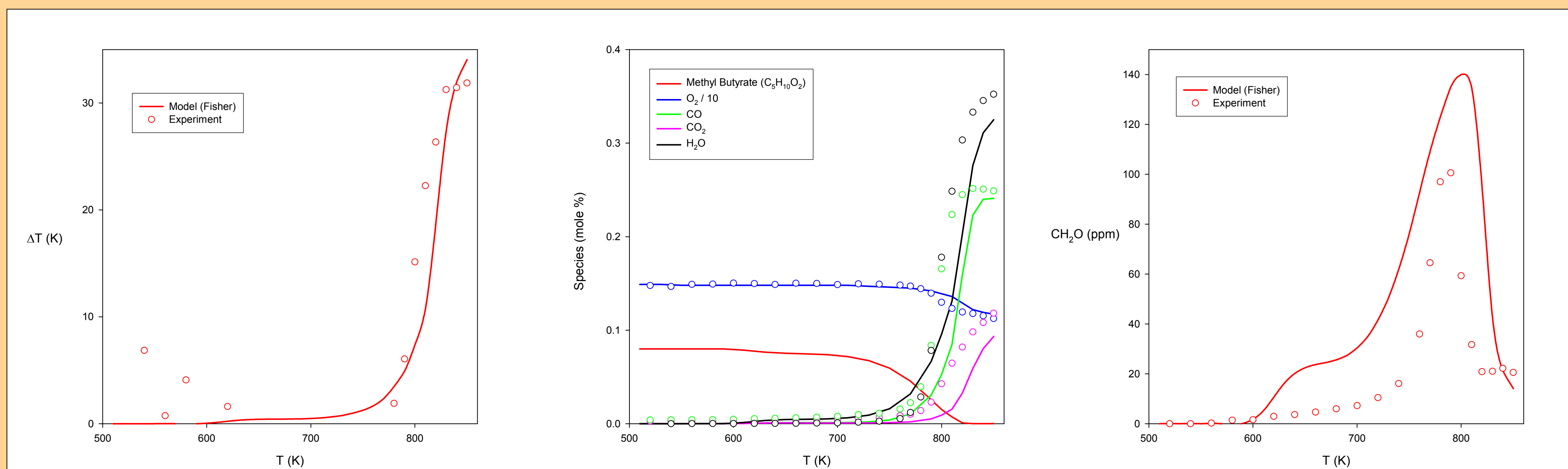## VPFR Reactivity Experiments and Comparison with Model

Figure 6. VPFR reactivity results and model predictions ($\phi = 0.35$, P = 12.5 Atm, $x_f = 800$ ppm, $\tau_{res} = 1.8$ s).
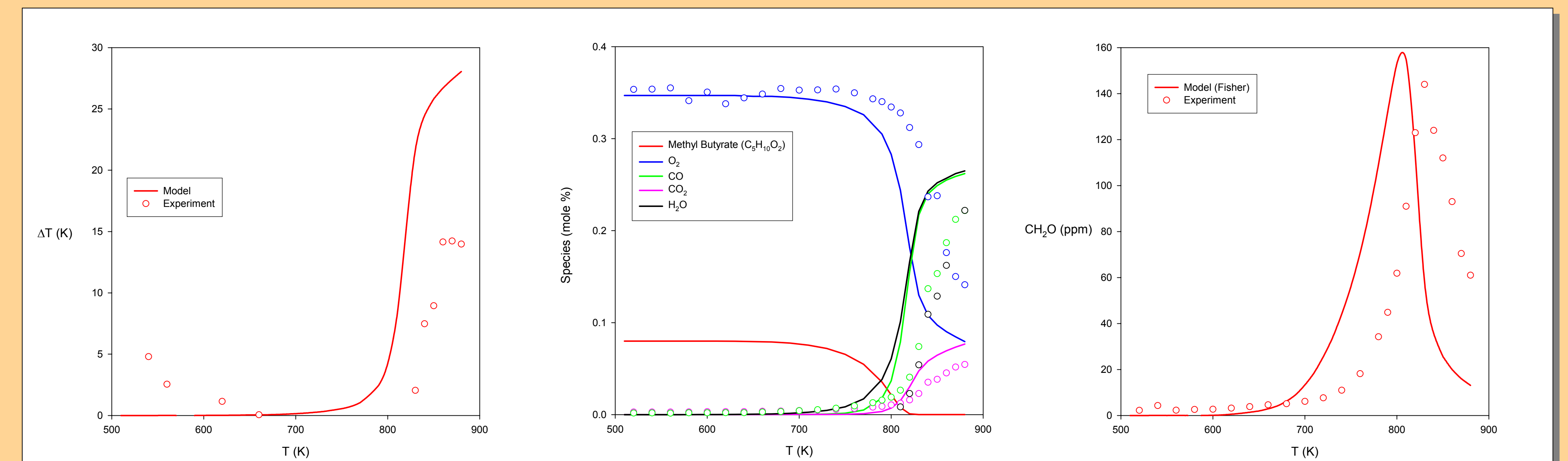

Figure 8. VPFR reactivity results and model predictions ($\phi = 1.5$, P = 12.5 Atm, $x_f = 800$ ppm, $\tau_{res} = 1.8$ s).
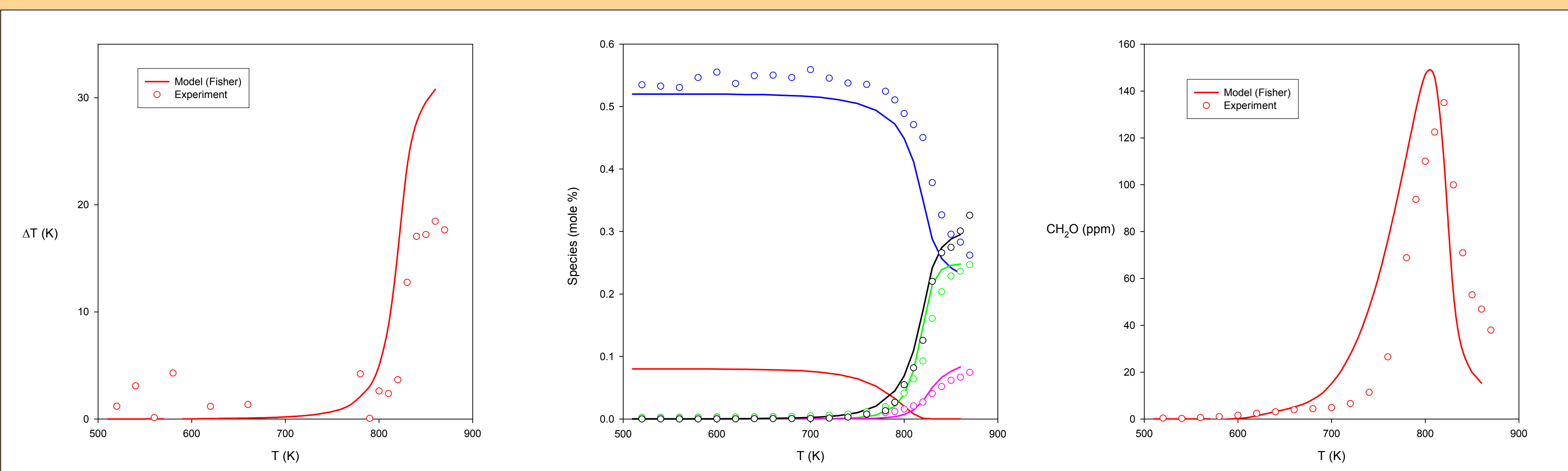

Figure 7. VPFR reactivity results and model predictions ($\phi = 1.0$, P = 12.5 Atm, $x_f = 800$ ppm, $\tau_{res} = 1.8$ s).

Results and Work in Progress

Figures 6 through 8 show the results of VPFR reactivity experiments along with Chemkin model predictions using the Fisher methyl butyrate mechanism[3] for fuel lean, stoichiometric and fuel rich conditions, respectively. As shown in Fig. 7 the predicted reactivity at stoichiometric conditions (as defined, for example by the CO_2 production) agrees well with experiments. The model underpredicts the observed reactivity at fuel lean conditions and overpredicts the observed reactivity at fuel rich conditions. While neither the model nor experiments exhibit a pronounced NTC region (at a residence time of 1.8 s), the formaldehyde production provides evidence of low temperature chemistry in both the model and experiments. The effect of low temperature chemistry is most pronounced at the fuel lean conditions of Fig. 6. Indeed, the predicted temperature rise shows a broad region of low temperature rise (< 1 K). While such a low temperature rise is difficult to measure experimentally, the measured formaldehyde profile shows evidence of low temperature chemistry.

The experiments conducted to date provide much needed experimental data against which to test existing biodiesel surrogate fuel mechanisms. However, since biodiesel fuels are typically blended with petroleum based diesel, there is also a need to better understand the chemical kinetic effects of oxygenated fuel blends. For example, Curran and coworkers[4] have numerically examined the chemical kinetic effects of adding methanol, ethanol, dimethyl ether (DME), dimethoxy methane (DMM) and methyl butyrate mechanisms to a previously developed n-heptane mechanism. However, there is a lack of data available against which to test these large mechanisms. Accordingly, work is in progress to perform flow reactor experiments of biodiesel surrogate/diesel surrogate fuel blends with the ultimate goal of reduced oxygenated fuel blend mechanisms that are small enough to use as a design tool in more detailed combustion studies.

References

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Acknowledgments

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