

Smart Carbohydrate Energy Carriers for Custom Transportation Fuel Synthesis.

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As a result of economic, environmental and legislative imperatives, the need to develop secure and sustainable alternatives to finite fossil derived liquid transportation fuels is urgent. One such promising alternative is the valorisation of readily available and abundant lignocellulosic derived hexose carbohydrates. Such hexoses may be configured as “smart” energy carriers by reaction with low energy density solvents, such as ethanol. Cellulosic derived glucose is the most naturally abundant hexose; but it has a propensity to form insoluble polymeric materials when used as reactant meaning that maximizing yields of biofuel components from glucose is very challenging. A viable solution to this problem is to promote the isomerization of glucose to fructose, which is easier to convert to potential fuel components in high yields. Consequently, extensive research is being conducted to induce this isomerization through a variety of homogenous [1] and heterogeneous [2] catalysts. However, comprehension of even basic reaction kinetic and mechanistic details of such systems is currently lacking, and thus represents one of the barriers to designing a viable process for fuel synthesis [3]. Another barrier to effective fuel synthesis is an appreciation of how the molecular diversity offered by such synthetic systems can be leveraged to produce fuel additives of adjustable properties to allow for blending with diesel or gasoline in a drop-in manner. To do this, a “one-pot synthesis”, without the need for expensive and difficult separations, is required.

To this end, this work establishes mechanistic and kinetic details of fructose hydrolysis to a range of biofuel components in a homogenous acid/ethanol system (“ethanolysis”).

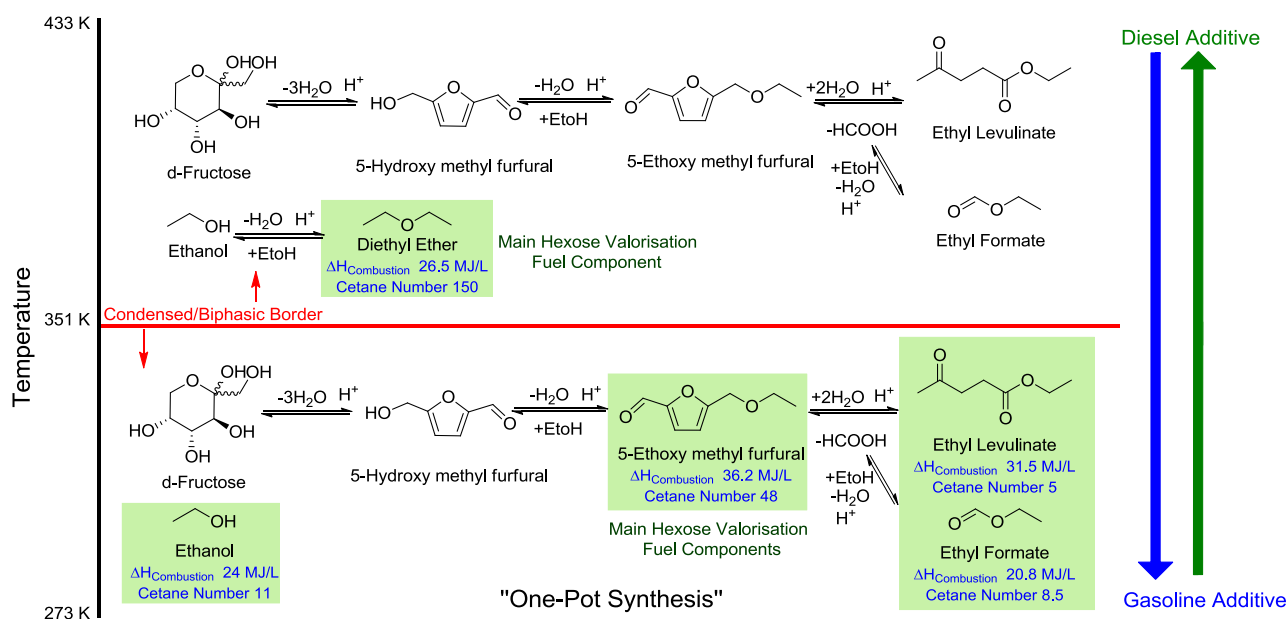


Figure 1. The chemical mechanism and fuel chemistry of a cellulose/ethanol synthetic fuel system interpreted as gasoline or diesel fuel additives.

Ethanol is chosen both as solvent and as a reacting partner with which to valorise by reaction with the hexose carbohydrate. Their reaction results in a varied set of fuel products that have energy densities and engine usabilities much improved with respect to ethanol, which is a relatively poor fuel by itself. Particularly, the ethanolysis process results in the formation of 5-ethoxy methyl furfural and ethyl levulinate as the main products. Ethyl levulinate can be used as a diesel blend additive at 20 volume % without modifications to existing diesel engines [4]. 5-ethoxy methyl furfural is yet more advantageous due to its high liquid density (36.2 MJ/L), which is comparable to that of petroleum derived diesel and gasoline [5]. In addition to these fuel components, depending on reaction conditions, the ethanol solvent can produce a “cocktail” of other exciting fuel components including diethyl ether and ethyl formate, (See Figure 1 and 2a) resulting in a tailorable fuel mixture that doesn’t require any separation or purification.

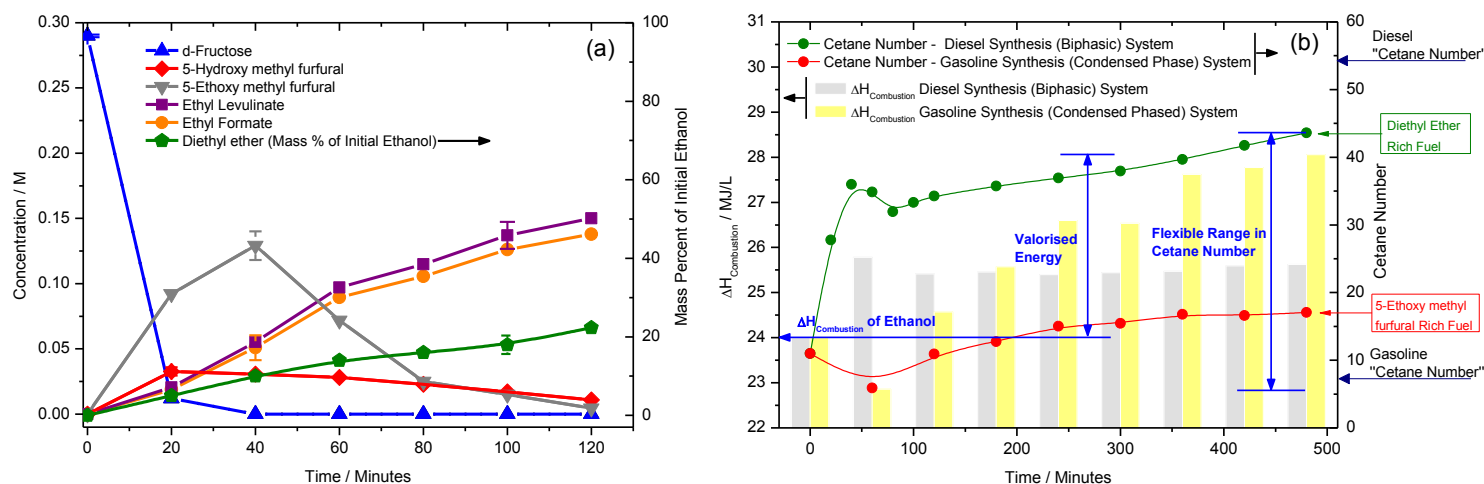


Figure 2(a): Measured species fractions from reaction of d-fructose in ethanol, (d-fructose/ H_2SO_4 0.01 M/0.29 M) at 453 K in a biphasic system. **Figure 2(b):** A comparison of the cetane numbers and energy densities of the flux of fuel components produced per time between condensed phase and biphasic reaction conditions.

This paper is organised across three core technical components:

- (1) Experimental derivation of ethanolysis species fractions in both condensed phase and biphasic conditions (see Figure 1).
- (2) Using the species fraction measurements to develop realistic reaction mechanisms (see Figure 2a), resulting in a robust kinetic model for the system.
- (3) Exercising the developed model to manipulate reaction conditions to produce drop-in fuel additives with tailor-made fuel and combustion properties (see Figure 2b).

Thus, a highly flexible process is developed to valorise hexose carbohydrates as “smart” energy carriers to produce specialised fuel additives in a one-pot synthesis.

References

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