Reducing Material Waste in Biodiesel Production through Multi-Energy Optimized Processing M.M. Kropf*

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ABSTRACT

Multi-Energy Optimized Processing is a patented green chemical processing technique which substitutes focused energy for hazardous chemicals to achieve efficient fuel conversions. Applied to biofuel production, this technology reduces material waste in the form of catalyst while improving energy efficiency providing a competitive advantage for the producers. The technology employs high intensity ultrasonics and microwaves to achieve rapid reaction rates while minimizing catalyst requirements. The reduction in catalyst not only reduces the waste associated with production, it also permits more economical treatment of "low-value" feedstock. The technology has been developed from bench top experiments to a continuous flow, pilot scale demonstration reactor. Scale-up validation studies have indicated the process is not capital intensive and suitable for plug-in upgrades to existing facilities. Finally, the insights gained in the development process has positioned this technology to have major impacts across a broad base of applications in the fuel and chemical processing arenas.

Keywords: green chemistry, process intensification, microwaves, biofuel, ultrasound

1 INTRODUCTION

The use of catalyst in current advanced biofuel production has fallen short of facilitating a green chemical process by complicating downstream processing and limiting feedstock choice ultimately raising costs. The current industry method of driving transesterification reactions involves using catalyst and excess amounts of reagents in long heated and stirred batch reactions. In the case of biodiesel production, the homogenous catalyst then becomes a contaminant in the glycerol co-product stream creating hazardous waste and reducing the value of the co-product. Furthermore, lower value feedstock such as used fryer oil or corn oil from dried distiller's grains contains elevated levels of free fatty acids. The presence of free fatty acids (FFA) in feedstock currently requires a second reaction step of acid esterification followed by a separation and neutralization step prior to the base catalyzed conversion of remaining triglycerides. Alternatively, producers can sacrifice the free fatty acids from the product stream by further elevating base catalyst levels and trapping the FFA's in the waste stream. This process inhibits producers from capitalizing on the reduced cost of waste stream feedstock by increasing the cost of treatment or reducing the efficiency of conversion; in both cases resulting in increased material waste.

To address this problem, green chemists have investigated ultrasonic cavitation, microwave heating, and supercritical technologies. Studies involving ultrasonic or microwave reactions have indicated reaction rate enhancements and supercritical techniques has offered a potentially catalyst free process. However, these processes typically require a large excess of reagents, co-solvents, and energy to maintain a large volume at extreme temperatures and pressures.

2 BACKGROUND

A novel technology termed Multi-Energy Optimized Processing (MEOP), developed at the Pennsylvania State University leverages the combination of microwaves and ultrasound to achieve energy efficient and robust green chemical process technology and demonstrated on the biodiesel production reaction. The success of this technology derives from advanced understandings of how each microwaves and ultrasound affects the chemical reaction efficiency.

2.1 Ultrasonic Emulsification

The key mechanism of improved chemical reaction rates and material efficiency surround high intensity ultrasonics is, in general, mass transfer. Specifically, the rate and degree at which two immiscible species are combined, which can be quantified by the size of dispersed phase droplets. In general, emulsions' stability are dictated by the size of dispersed phase droplets. Specific to chemcial reactions bewteen imisscible species, this degree of stability correlates with the degree of mass transfer facilitateed. In this work, it was measured that the degree of emulsidication, and thereby the degree of mixing, was optimized through the selection of specific high intensity ultrasonic frequencies. Higher frequency ultrasonics, within the limitation of actuators to produce sufficient mechanical oscillations, resutled in smaller dispersed phase droplets than lower frequency ultrsounds and both smaller and broader range of droplet sizes than high speed shear mixers.

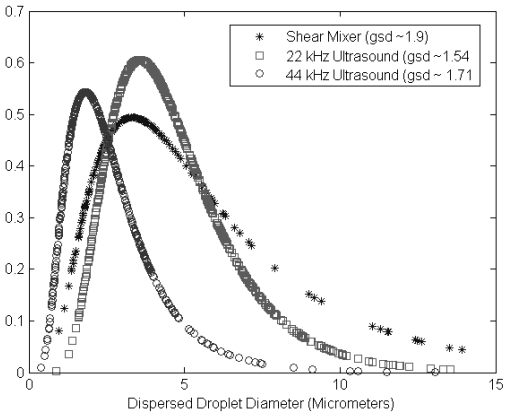

Figure 1: The dispersed phase droplet diameters geometric standard deviation and mean value decrease to optimal values at increased ultrasonic emulsification frequency. [1]

2.2 Microwave Superheating

The key mecahnism of microwave heating that results in improved reaction rates and material efficiency is the nature in which materials absorb, or exhibit loss to, electromagnetic waves. In particular, different types of chemicals will absorb different frequencies of microwaves to different degrees. This is quantified by the complex pertmittivity of a material and measured by dielectric spectroscopy. In biofuel production, three main mechanicsms of dielectric loss are found in typical feedstock and reagents. Homogenous catalyst, undergoes an ionic conduction loss increasing with lower frequencies of microwaves (specfically less than 1 GHz). Polar solvents, such as methanol, absorb based on the Debeye relaxation of polar molecules. Unlike ionic conduction, this mechanism of loss centralizes at microwave frequencies specific to the polar molecule. Finally, uniform dielectric loss from natural oils and similar feedstock has a relatively low dielectric loss without variance over the microwave frequency spectrum.

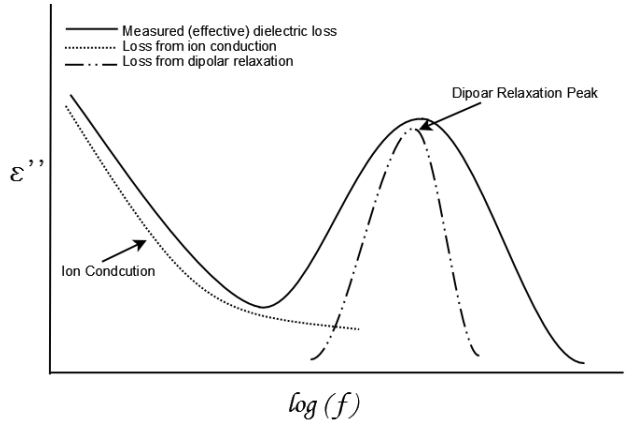

Figure 2: Shows the absorption properties of specific chemical species in terms of microwave frequency. [2]

The result of variable mechanisms for microwave absorption is two fold. One, it follows that a specific reagent in a reaction, or more specfically a particular bond structure, can be selected for the introduction of energy selectively. Second, the heating rates pre-determined by thermodynamics and fouriers heating equations are circumvented by the introduction of a heating rate term tied directly to the magnitude of incident electromagnetic energy. This feature permits the phenonmenon of microwave super heating, in which a material is elevated in temperatuer beyond the boiling point prescribed by the ambient pressure. This superheated state can be further extended by the stabilization of the selected microwave absorbing species in an ultrasonically formed emulsion. The result of the optimization of this paramter allows for the selection of microwave frequencies to coincied with the selective introduction of energy into a species stabilized and throroughly mixed with other reactants. [2]

3 RESULTS

The results of this effort have indicated improved reaction rates with less catalyst. More-over, the extent of additional catalyst and methanol to address feedstock with elevated Free Fatty Acid (FFA) content was eliminated altogether. This results in a process that uses less energy and materials to process biofuels in a continuous flow fashion.

3.1 Reduction in material waste

At scale, this technology has achieved ASTM specification biodiesel conversion at 30 Gallons per hour with a fraction of the industry accepted amount of homogenous base catalyst (0.2% by weight as compared to 0.5% by weight). Furthermore, this technology has been demonstrated on feedstock with elevated free fatty acid content without the need for additional catalyst or acid esterification pretreatments.

3.2 Pilot scale implementation

After preliminary bench scale measurements, a system was designed to function at pilot scale, continuous flow scales. Starting at 10 gallons per hour (GPH) with capacity to reach 60 GPH, the system's design methodology and scale-up procedure were identified, deomonstrated, and verified for each component technology: microwaves and ultrasound. The current limit of 60 GPH is based soley on the capacity of the pumps integrated into the pilot plant. No major limitations of the technologies, microwaves and ultrasound, were realized in the scale up development undertaken in this study. Furthermore, no theoretical limits due to scale were identified. In short, the economy of scale

for Multi Energy Optimized Processing is in the worst case linear.

4 CONCLUSIONS

Research into the deployment of the MEOP technology for biodiesel production has included to the design, construction, and validation of a pilot scale demonstration reactor. The design of this reactor administers microwaves and high intensity ultrasound in a highly efficient and novel manner to a continuous flow of reagent streams. In addition to the reduction in catalyst, MEOP technologies achieve an increase in energy efficiency as compared to the reactor component of a conventional system. The estimated capital costs of commercial plants are competitive with existing technologies.

4.1 Waste Reduction in Biofuel Production

The development of MEOP technology has resulted in an understanding which makes MEOP poised to improve the energy efficiency and reduce the material waste of a variety of fuel and chemical processes. The potential is no less than to facilitate a consolidated, robust, and sustainable approach of commercial biofuel production.

4.2 Development of Platform Technology

Finally, the resulting demonstration of microwaves and ultrasound as a viable industrial scale green technology will impact the broader chemical processing industry, specifically the transportation fuels sector.

REFERENCES

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