This paper will discuss: RC1 experiments elucidating the role of headspace recirculation, Gas/Liquid mathematical modeling predictions based on RC1 results and a novel agitator retrofit, the ML-4 gas inducing agitator, which has been demonstrated commercially to reduce overall gas consumption while improving product quality.

**Keywords:** Hydrogenation, mixing, headspace, modeling, liquid/gas reaction, mass transfer, reaction rate.

Batch oil hydrogenation processes are complex multiphase reactions. The efficiency of gas/liquid mass transfer in these processes is oftentimes critical in determining the observed overall reaction rates and product selectivities. Impurities in the hydrogen feed gas can accumulate in the reactor headspace, reducing process rates and altering product specifications. A typical solution to this problem is to periodically vent headspace gases or operate reactors with reduced liquid volumes. This approach wastes hydrogen and is capable of reducing overall plant capacities. A better approach is to actively recirculate the headspace gas back into the reaction mixture. This paper will address the impact of gas mixing and hydrogen purity in batch oil hydrogenation processes via three different methods:

1) experiments utilizing the METTLER TOELED RC1 HP60 reaction calorimeter,
2) mathematical modeling results,
3) a proprietary agitator retrofit, the ML-4, designed to promote enhanced mass transfer in gas/liquid systems.

All experimental results were obtained with the use of a METTLER TOELED RC1 and an on-line FTIR system used to monitor chemical intermediates as a function of reaction time. Our experimental studies examined three different purities of hydrogen gas mixtures:

1) 99.9995 % $\text{H}_2$,
2) 95 % $\text{H}_2$, 5 % $\text{CH}_4$,
3) 95 % $\text{H}_2$

with the rest of the impurity containing amounts of a number of different compounds including methane, carbon monoxide, nitrogen, and carbon dioxide. The impure hydrogen gas mixtures were purposely chosen to reflect representative feed streams exiting old steam methane reformers. In addition to hydrogen gas purity, this paper also examined the effects of pressure, agitation intensity and two different liquid/gas volume ratios. The variables held constant in our experiments were the feedstock (refined, bleached and deodorized soybean oil), catalyst (Engelhard’s E-470D selective hydrogenation catalyst) and temperature (160°C).

Results from experiments clearly illustrate that the highest reaction rates are obtained with the highest purity hydrogen feedgas. Lower rates are shown for the impure feedgas mixtures due to the buildup of impurities in the reactor headspace, thus decreasing the partial pressure of hydrogen in the headspace. If, at this point, the headspace is vented and fresh feedgas introduced, the reaction rate does increase but eventually decreases due to the buildup of impurity. In particular, results for the 95% $\text{H}_2$ with CO mixture yield similar reaction patterns with lower overall reaction rates. Also, ventings do not cause reaction rates to increase substantially. This is primarily due to carbon monoxide poisoning of the nickel catalyst. In addition to reaction rate, the hydrogen purity also has a significant effect on product selectivity, namely the amount of bans isomer found in the partially hydrogenated oil. Infrared spectroscopy results confirm that the highest
purity hydrogen feedgas produces the lowest amount of bans for the conditions studied while the hydrogen gas mixture containing CO produces the most amount of bans isomer at all values of conversion. Therefore, our studies showed that, in addition to decreasing overall reaction rates, impurities in the hydrogen feedgas also may produce more unwanted bans fatty acids.

In addition to the effect of hydrogen purity, other experiments confirmed the beneficial effects of higher pressure and enhanced mass transfer on reaction rates. However, experiments that were conducted at higher pressures utilizing gas mixtures containing impurities, specifically carbon monoxide, show negligible reaction rates. In these cases, higher pressure, which usually increases reaction rate, actually forces the carbon monoxide onto the catalyst particle faster, thereby poisoning the catalyst. Venting the reactor and reducing the pressure does cause the reaction rate to recover somewhat, but eventually the carbon monoxide does succeed in poisoning the catalyst again. Additional experiments proved that this catalyst poisoning could be reversed; if the reaction system was vented and the feedgas switched to 100% pure H₂, the reaction rate increases dramatically, approaching a quantitative value comparable to previous reactions where the catalyst was never poisoned. These experiments demonstrate that catalyst activity can be recovered with little consequence if pure hydrogen feedgas is used.

In addition to experiments, mathematical modeling was also used to explore the effects of hydrogen purity, mass transfer and pressure on reaction rates and product selectivities. Our mathematical model utilizes many of the more relevant parameters demonstrated to be of importance in a gas/liquid reaction system. These parameters are incorporated into a series of detailed mathematical equations which are written for the three species of interest, namely the hydrogen gas, the inert gas, and the substrate. Without examining each equation term by term, these equations utilize several parameters mentioned previously in the experimental portion of this paper, such as the gas/liquid mass transfer coefficient, the residence time of the gas phase in the headspace gas, the residence time of the gas phase in the dispersed gas phase, as well as the reaction rate constant. The independent variables in the model were manipulated to discern their effect on the dependent variables. The five independent parameters of interest that were varied in the modeling studies included the following:

1) the fraction of inerts in the feedgas, thus simulating different hydrogen purities,
2) the ratio of the liquid volume to the headspace volume,
3) the gas/liquid mass transfer coefficient,
4) the feedgas pressure,
5) the residence time of the gas in the headspace volume.

The values or ranges over which each of these variables were manipulated were chosen to benchmark previous experiments. In short, results from mathematical modeling studies confirmed previous experimental findings and illustrated the beneficial effects of high purity hydrogen feedgas, high pressure and enhanced mass transfer conditions. Modeling results also emphasized the important role of headspace turnover ratio or the residence time of the gas in the headspace volume before it becomes reincorporated into the dispersed gas phase. For lower residence times, or what translates into higher headspace turnover ratios, the reaction finishes significantly faster than for higher residence times or lower headspace turnover ratios.

The last portion of this presentation focuses on APCI's new propriety agitator, the ML-4. This agitator is capable of being retrofitted to most conventional agitators in operation today. Essentially the ML-4 is a set of 4 hollow L-tubes affixed to an agitator shaft via central hubs and swagelock connections. The top portion of the L-tubes are open to the headspace gas, while the lower portion of the tubes are submerged in the liquid phase. As the central agitator shaft spins, the L-tubes also rotate, creating a high tip speed and a low pressure zone at the outlet of the tubes. By Bernoulli's principle, this pressure difference results in gas being drawn down from the headspace back into the liquid volume, preferably in high shear zones. The specific design of the ML-4 can be customized for essentially any reactor configuration with the aid of computation fluid dynamic modeling which seeks to optimize the performance of these draft tubes by placement of these tubes in the reactor, the tip-to-tip distance, the submerged depth and the tube diameter. Some of the potential advantages of this type of agitator retrofit, as compared to others in the industry, are that it is relatively inexpensive, additional power is usually not required and the existing gear box and reactor seals do not need to be replaced.

A short video illustrates the effectiveness of the ML-4 agitator retrofit versus a conventional agitator system. Studies were conducted for an air/water
system in a 200 gallon plexiglass tank equipped with heating coils. Two different agitation configurations were studied. While both tanks are equipped with a six-bladed Rushton turbine at the bottom of the tank and a four-bladed pitch blade near the top of the tank, the tank on the left also possesses the ML-4 agitator retrofit. As can be shown by visual examination in a side-by-side comparison, the tank equipped with the ML-4 retrofit has a finer bubble size distribution with a higher volume of gas being held up more evenly throughout the volume of the tank. This mixing pattern would result in a higher gas/liquid surface area available for mass transfer and hence, a greater gas/liquid mass transfer coefficient, kla.

In summary, this paper examines the complex interaction that exists among a number of key process variables important in a gas liquid mixing system, namely the kla or gas/liquid mass transfer coefficient, the headspace gas turnover ratio, the pressure and purity of the hydrogen feedgas as well as the liquid/gas volume ratio. Both experimental and mathematical modeling results confirmed that the purity of hydrogen feedgas is critical in achieving desired productivity and selectivity goals. Impurities in the hydrogen feedgas can build up in the headspace, necessitating costly and wasteful venting procedures. Poisons such as CO contained in an impure hydrogen feedgas can render nickel catalyst essentially useless. Using high purity hydrogen, in conjunction with APCI’s new appropriately agitator retrofit, the ML-4 has been shown to lower bans isomer content, decrease overall hydrogen consumption as well as maintain and in some instances even increases productivity.