

Utilizing the Film Boiling Process to Promote Chemical Change of Organic Liquids

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ABSTRACT

This presentation outlines a unique approach to converting organic molecules to alternative substances by film boiling. The process is illustrated by conversion of methanol (CH_3OH , boiling point (bp) of 338K) and ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$, bp of 467K) to synthesis gas (a mixture of CO and H_2). A theoretical model for film boiling with chemical reaction is discussed and an experimental design to measure product yields for film boiling on the outside of a horizontal tube is presented. The process of chemical reaction by film boiling is termed a Film Boiling Reactor (FIBOR). The FIBOR operates as follows.

A solid surface such as a horizontal tube is immersed in a subcooled liquid. The tube is heated to create a high surface temperature that transitions heat transport from single-phase convection to nucleate boiling and eventually to film boiling. In the film boiling regime a stable vapor layer surrounds the surface. As the vapor within the film flows over the heated surface, it reacts either by decomposition if the tube is bare or catalytically at the tube wall if the tube is coated with a suitable catalyst. The gases, which consist of unreacted vapor and products, collect at the top of the tube where bubbles form, detach and percolate through the liquid pool under the action of buoyancy in a manner typical of film boiling.

Features of the FIBOR include the following: the reactor would essentially build itself (i.e., it is self-assembled) as a consequence of transitioning from nucleate to film boiling as the temperature of the heated surface is raised; stability of the reaction volume is guaranteed by the natural balancing of heat transfer from the solid surface with vaporization at the liquid/vapor interface; versatility to promote conversion by both thermal decomposition or catalytic means; with one boundary of the reaction volume being 'hot' (solid side) and the other 'cold' (liquid/vapor interface side) so that high temperature reactions can occur in a relatively low temperature supply liquid; and a range of organic molecules may be converted

including heavy organics formed as a by-product of developing bio-derived liquids (e.g., bio-diesel from non-food feedstocks).

The experimental design employs a horizontal, electrically heated rod (Inconel 600) submerged in a pool of the reactant liquid. The design provides for control of the rod surface temperature, bulk liquid temperature, reflux of the condensate and analysis of the chemical species by gas chromatography. Film boiling is initiated in a procedure that minimizes liquid contact with the rod prior to film boiling, as direct solid/liquid contact would deactivate the platinum-based catalyst coatings employed in the experiments. In addition to the experiments, film boiling theory is extended to include chemical reaction in the vapor film along with radiation across the vapor film, liquid subcooling and liquid motion.

Results are shown that illustrate the variation of product yields - dominated by CO and H₂ for methanol and ethylene glycol conversion processes - with tube wall temperature and subcooling. Catalytic reaction for methanol resulted in yields on the order of 104 L/min/m² at temperatures between 800K and 1300K (the highest employed for methanol) for the 5 mm diameter by 150 mm long tube used. For ethylene glycol at the higher tube wall temperatures imposed, catalytic reaction gave comparatively lower yields than methanol at comparable temperatures. Product gases from catalyst-coated tubes for ethylene glycol were most likely generated by a combination of thermal decomposition and catalytic reaction, unlike methanol, because of the higher threshold temperature for catalytic conversion of ethylene glycol.

A simplified model for film boiling with chemical reaction, based on assuming a single step reaction, is used to qualitatively explain the experimental trends and to infer rate constants of the assumed reactions. It is shown that the effect of liquid motion appears to be small as is radiative absorption within the vapor film compared to radiation across the film. The effect of radiation on product yields and vapor film thickness is in any case small for the range of tube wall temperatures examined. Activation energies extracted to give the best agreement with methanol yields showed an unusual dependence on temperature. This result suggests that the assumed single step reaction may have to be supplemented by a multi-step sequence.