



On using film boiling to thermally decompose liquid organic chemicals: Application to ethyl acetate as a model compound



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ABSTRACT

Film boiling on a horizontal tube is used to study the thermal decomposition of ethyl acetate. The decomposition process is driven by the high surface temperatures that are typical of the film boiling regime that can promote chemical change of superheated vapors in a low temperature liquid. The decomposition products are carried away from the tube by vapor bubbles formed at the top of the tube that then percolate through the system. For the experiments reported here, the bulk liquid is stagnant, the liquid is slightly subcooled, and bubble transport is entirely by buoyancy.

The results show that the primary decomposition products are acetic acid and ethylene in proportions consistent with the accepted unimolecular decomposition pathway for ethyl acetate. While ethylene is a non-condensable product gas, acetic acid is miscible in ethyl acetate and small amounts of it were detected in the bulk liquid after four hours of operation. The resulting binary (ethyl acetate/acetic acid) phase equilibrium behavior of the reactant pool contributed to trace amounts of carbon dioxide and methane being found in the product gas from acetic acid decomposition that had preferentially vaporized in the film.

The minimum film boiling temperature of ethyl acetate was measured to be approximately 711 K. Up to about 1000 K the product yields showed a comparatively small variation with average tube temperature, while above 1000 K the exhaust gas flow rate was substantial and increased in an approximately linear fashion with tube temperature. Methane and carbon dioxide were also detected in the product stream owing to acetic acid decomposition, though the amounts were comparatively small. The results show the viability for film boiling to promote decomposition in a controlled way to products consistent with those expected from the reactant molecule.

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1. Introduction

Chemical conversion of condensed phase organic molecules to lighter fractions requires pre-vaporizing the reactant, which is typically accomplished in a process separate from the reactor, after which the reactant gas is transported to the high temperature reaction environment (e.g., flow [1], opposed jet [2,3], jet-stirred [4], and monolith chemical [5,6] reactor configurations, etc.). Alternative concepts have been developed that more closely couple pre-vaporization and transport. A number of the designs employ partial catalytic oxidation to provide for autothermal operation without external heat input owing to the exothermicity of the oxidative conversion process. For example, one design involves partial oxidation inside a tube of a gaseous reactant flowing within a porous platinum support positioned in the tube [7]. Air is pumped through

the porous tube on one side and gaseous reactant is supplied by vaporization of the reactant liquid on the other. Other concepts that use vaporization of a liquid to transport the reactant gas include spray injection of a hydrocarbon into a cylindrical tube to coat the tube walls with the liquid, and subsequent evaporation of the liquid film by external heat addition to the tube [8–10]. The reactant gases that flow through a catalyst honeycomb are then partially oxidized.

Vaporization of droplets that impinge on a surface has also been used as a means to develop a gaseous reactant such that the droplets are levitated above the surface as in the classic Leidenfrost phenomena [12]. The vapors underneath the droplet may react homogeneously in the vapor film that separates the liquid from the solid, or the vapors may flow into a porous catalytic substrate [13,14] and heterogeneously react on the surface of the pores to form products [11]. This latter process also forms the basis of a droplet impingement reactor concept described by Varady [15].

The present paper employs a reactor that relies on evaporation of a liquid to both provide the reactant gas supply and to define the

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Nomenclature

| | | | |
|-------------|--|----------------------|--|
| A_i | coefficient of the trend line in Fig. 10 | R | radius of the heater tube (m) |
| a_i | coefficient of the calibration curve ($\text{mL min}^{-1} \text{V}^{-2}$) | R' | characteristic length for horizontal cylinders |
| B_i | coefficient of the trend line in Fig. 10 (K) | \bar{R} | gas constant ($\text{cal mole}^{-1} \text{K}^{-1}$) |
| b_i | coefficient of the calibration curve ($\text{mL min}^{-1} \text{V}^{-1}$) | t | time (s) |
| C_i | coefficient of the trend line in Fig. 10 | T | temperature (K) |
| C_{pi} | product concentration of species i (M) | T_b | normal boiling temperature (K) |
| C_R | reactant concentration (M) | T_w | tube wall temperature (K) |
| c_i | coefficient of the calibration curve (mL min^{-1}) | y_i | molar fraction of a single gas in the product gas stream |
| d_o | outer diameter of heater tube (m) | V | flow meter output (V) |
| d_i | inner diameter of heater tube (m) | \dot{V} | volumetric flow rate of a mixture gas (mL min^{-1}) |
| E_a | activation energy (cal mole^{-1}) | \dot{S}_i | calibration relation of a single gas (mL min^{-1}) |
| g | gravity (m s^{-2}) | q'' | heat flux (W m^{-2}) |
| h_{fg} | heat of vaporization (kJ kg^{-1}) | q''_{\max} | critical heat flux (W m^{-2}) |
| H_c | heat of combustion (kJ kg^{-1}) | | |
| I | current (A) | | |
| K | reaction rate (s^{-1}) | Greek letters | |
| L | tube length (m) | δ | vapor film thickness (m) |
| N | number of product gas species | ρ | electrical resistivity ($\mu\Omega \text{m}$) |
| \dot{N} | molar flow rate of a mixture gas (mole s^{-1}) | ρ_l | liquid density (kg m^{-3}) |
| \dot{n}_i | molar flow rate of the individual non-condensable gases (mole s^{-1}) | ρ_v | gas density (kg m^{-3}) |
| P | Pressure (atm) | σ | surface tension (N m^{-1}) |
| Q_{in} | power supplied to the heater tube (W) | | |

actual reactor volume in a sort of self-assembled manner. The transport dynamics of such a reactor were analyzed [16,17], and subsequently shown to be capable of converting several organic species to products [18,19] including methanol and aqueous ethylene glycol mixtures to synthesis gas (a mixture of CO and H₂) as the primary product. Carbon formation was noted for the pure organic while it was reduced significantly for the aqueous mixtures. Both catalytic (surface reaction on platinum and nickel catalysts) and homogeneous gas phase processes characterized the conversion process.

The complexity of the molecules thus far examined by film boiling has made it a challenge to infer the reaction pathways from measurement of the exhaust gas composition. While ethylene glycol and methanol decompose to synthesis gas as the primary products, detection of methane and carbon dioxide in the exhaust gas, as well as carbon formation on the heater surface suggests additional conversion steps.

In the present study, the thermal decomposition of a model compound for which decomposition is expected to be particularly simple is examined: ethyl acetate (EA, CH₃COOC₂H₅, normal boiling point of 350 K). EA is known to decompose in a single step into two products (acetic acid and ethylene) with a known rate constant [20–24] so that measurements of product yields should ultimately be valuable for validating models of film boiling (e.g., [25–29]) to include chemical reactions [16,17]. In addition, the limited number of product gas species for ethyl acetate decomposition facilitates developing calibration correlations in the experiment for converting electronic information (e.g., voltage) from digital flow meter output to flow rates. EA also has several industrial applications, including its use as a solvent and as a hardener in paints.

Non-oxidative (pyrolytic) conversion of ethyl acetate is being examined, so that the conversion process requires a net energy input to maintain a steady decomposition process. This is accomplished in the present study by employing an electrically heated horizontal tube as the geometry used to support film boiling and the reactor volume (the vapor film). The tube is mounted in a pool of the reactant liquid which is maintained close to its saturation temperature. Film boiling is established by heating the immersed tube to promote a natural progression of heat transfer modes as

the liquid transitions from single phase convection to nucleate boiling and ultimately through the critical heat flux (CHF) condition to film boiling where a stable vapor film surrounds the tube. Fig. 1 is a schematic of this configuration. In film boiling, the insulating effect of the vapor produces a large temperature drop between the high tube surface temperature and the comparatively colder liquid/vapor interface which is at the saturation temperature. The conversion process occurs within the vapor film at rates commensurate with the local temperature and the concentration of reactant gases.

Gases flowing in the film collect at the top of the tube where bubbles form, detach and percolate through the liquid pool (under

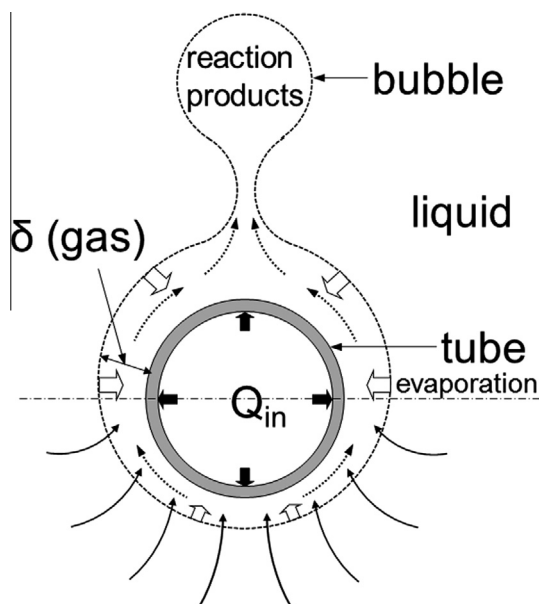


Fig. 1. Schematic cross-sectional view of film boiling on a horizontal tube.

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