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Thermal and catalytic decomposition of aqueous ethylene glycol mixtures by film boiling

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ABSTRACT

Aqueous ethylene glycol (EG) mixtures are decomposed by film boiling at near saturation temperatures on a horizontal tube in a stagnant pool containing up to 20% (volume) water. The reactor volume is the vapor layer that blankets the tube in the film boiling regime. Chemical reactions are promoted within the vapor film by the tube temperatures while the bulk liquid is close to its bubble point temperature. Experiments are carried out on bare tubes and tubes coated with nickel and platinum catalysts to show the effects involved.

Results show that chemical conversion of the hydrocarbon vapors produces primarily CO and H_2. Product yields (flow rates) are enhanced on a catalyst, with an 80%EG/20%water mixture (volume percent) showing three to four times higher product yields compared to a bare tube. Platinum coatings showed slightly higher yields than nickel coatings.

Diluting ethylene glycol with water decreases the overall chemical reactivity owing to preferential vaporization of water that enriches the film with steam. The presence of steam in the vapor film appears to reduce carbon deposition or "coking" on the tube when enrichment by steam is significant: deposits were observed for pure EG and 90%EG/10%water mixtures but not for 80%EG/20%water mixtures.

1. Introduction

It has recently been shown that single component liquids can be converted to lighter fractions by using the film boiling process [1–4]. The concept exploits the insulating effect of a vapor film surrounding a heated surface in film boiling to raise gas phase temperatures at the solid surface to levels that can promote thermal decomposition while maintaining the vapor film. Fig. 1a is a schematic of the process for the configuration of a horizontal tube.[3]

With film boiling, a vapor layer (of thickness δ) is created on the tube surface. The comparatively low thermal conductivity of the gas results in temperatures that range from T_w at the tube surface, to T_{sat} at the liquid/vapor interface. This temperature difference can be over a thousand degrees. Considering that many organic vapors will thermally crack or decompose when exposed to such temperatures, the high temperatures in the vapor layer have the potential to drive chemical reaction in a cold bulk liquid. We have termed the volume bounded by δ a film boiling reactor or "FIBOR" [1,5]. Its operational boundaries are governed by the boiling curve of a liquid. In the film boiling regime, the energy input to the tube (or heat generated by Joule heating) must maintain the vapor film and support the reaction, which is typically endothermic for organic vapors. Fig. 1b schematically illustrates the energy transport paths for film boiling with chemical reaction. If the vapor film is not maintained or the surface temperature is too low, the chemical reaction process ceases.

The FIBOR conceptually has several unique features compared to conventional plug flow or packed bed reactors: it essentially builds itself by the natural transition of heat transfer modes when a surface is heated in a liquid pool, from single phase convection, to nucleate boiling, the critical heat flux (CHF) condition and ultimately film boiling; high temperature conversion occurs in a cold bulk liquid because of the insulating affect of the vapor film, which mitigates high temperature containment issues of conventional reactor systems [6]; the reactor design is simple as it involves no moving parts (e.g., pumps to transport the reactant through the reactor, which for the FIBOR occurs by evaporation at the liquid/vapor interface); products are transported by bubbles under the action of buoyancy (a variant could develop the reactor in forced convection film boiling); the FIBOR is inherently portable as it requires only that a heated surface be inserted into a liquid pool to

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[3] The horizontal tube is employed because of its simplicity to develop an experimental design and model the process. The concept also applies to other geometries on which film boiling could be established.

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Nomenclature

A	area, m^2
E	activation energy, $J\ mol^{-1}$
k	chemical reaction rate, s^{-1}
I	current, amp
L	length, m
$\dot{m}$	mass flow rate, $kg\ s^{-1}$
Q	heat transfer, W
q''	heat flux, $W\ m^{-2}$
R	electrical resistance, Ω, universal gas constant, $J\ mol^{-1}\ K^{-1}$ or tube radius, m
T	temperature, K
T_r	approximate temperature below which the product yield is very low

Greek Letters

δ	vapor layer thickness, m
ρ	electrical resistivity, μΩ m
φ	mass fraction

Subscripts

in	transport inward
m	minimum film boiling temperature
sat	saturation
s	solid
w	wall
∞	bulk liquid

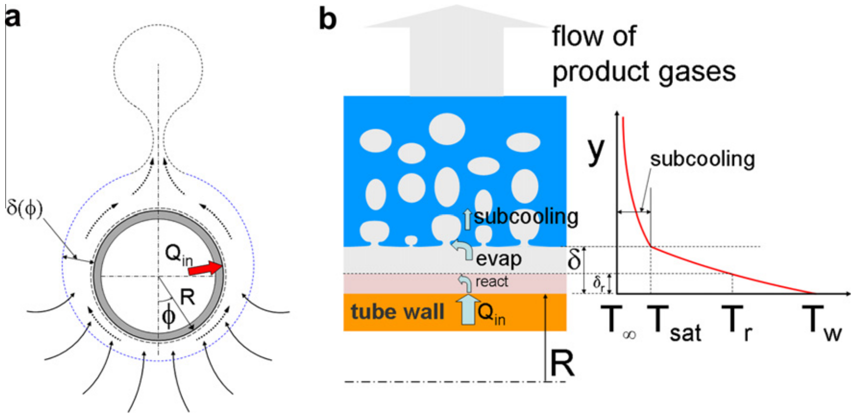

Fig. 1. Schematic of a FIBOR configuration for a horizontal tube. (a) Tube viewed on end; the reaction zone is the volume bounded by the blue dotted line and the tube surface. Arrows indicate gas flow (dotted) and liquid flow (solid) paths. (b) View on plane. Reaction will occur in the shaded volume bounded, $0<y<\delta_r$. Outside of δ_r where $T_w < T_r$, the temperature is too low for reaction. Arrows indicate heat flow paths for reaction, evaporation and subcooling. Not to scale.

affect conversion of the fluid (i.e., this means that the reactor could easily be brought to the reactant thereby allowing for in-situ conversion); and it is potentially scalable.

These advantages are offset by the lack of flexibility of the FIBOR compared to conventional systems (e.g., plug flow or static reactors). The control variables are tied by the dual requirement to maintain the vapor film and to ensure that enough heat enters the system to maintain the reaction (thermal decomposition is typically an endothermic process). If the surface temperature is too low the film will destabilize and the FIBOR will be destroyed (the low end to the film boiling regime is governed by the so-called "Leidenfrost" point [7]) or the reaction will not occur at an appreciable rate to make the concept viable; it is possible for the vapor film to exist but that the surface temperature would be too low for a reaction. In addition, the residence time of reactant molecules in the reactor itself (i.e., the vapor film) is not independently controlled.

The volume bounded by δ in Fig. 1b is not the full volume for chemical conversion. In reality, a reaction will proceed at an appreciable rate only when the temperature is above a threshold value, T_r. The decomposition process will be confined to a smaller volume bounded by $0 < y < \delta_r$. As a result, decomposition by film boiling must occur at locally higher apparent temperatures than conventional reactors where the temperature is uniform throughout, but nonetheless at lower average gas temperatures.

Previous work investigated the performance of a FIBOR for pure liquids (e.g., methanol and ethylene glycol (EG), $C_2H_4(OH)_2$, normal boiling point of 467 K) [1]. EG, in particular, is widely used as an anti-freeze, in hydraulic brake systems, in some paints, plastics and adhesives, and as an aircraft de-icer. Furthermore, EG has been used as a model fuel for pyrolysis oil in pilot scale flow reactors [8,9].

The complexities associated with film boiling of miscible mixtures coupled with chemical reaction have not previously been explored. This is an important issue because in many practical systems the reactant liquid is a mixture. The present study considers this problem for aqueous EG mixtures. With water mixed with EG, the gas composition in the film will be enriched by water as illustrated by the bubble point curve shown in Fig. 2 [10]. Product yields should therefore be lowered as a result. It is anticipated that above a threshold water dilution the product yields would be too low to be measured with the instrumentation used.

The experiments are carried out at atmospheric pressure at low bulk liquid subcoolings. Measurements are reported of the boiling curve which determines the operational domain of the FIBOR, and product gas flow rates produced by conversion in the vapor film. The species produced by decomposition are identified by gas chromatography analysis and the reaction steps are inferred by the species that are found in the product stream. The primary variables are the water concentration and tube surface temperature.

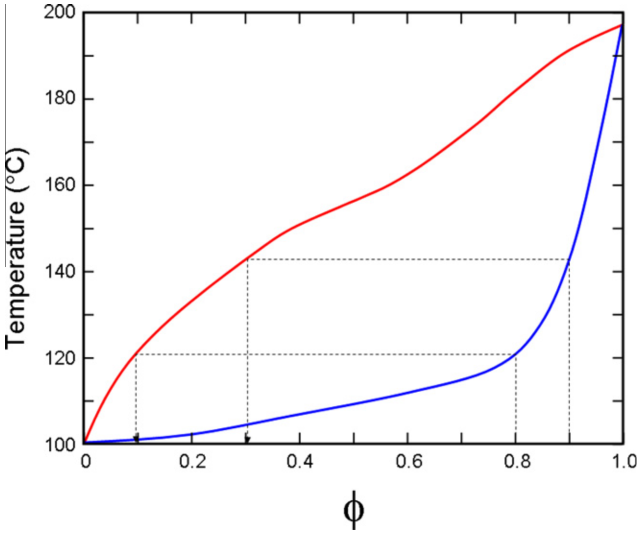

Fig. 2. Phase diagram for ethylene glycol/water mixtures at atmospheric pressure (adapted from [10]). Dotted lines indicate the liquid (blue) and vapor (red) compositions. φ is the mass fraction of ethylene glycol in the mixture. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

In addition to examining mixture effects for polished bare tubes, film boiling on catalyst-coated tubes is examined. Tubes coated with Pt and Ni catalysts offer the potential for increasing product yield for a given temperature. The highest water concentration examined is 20%, as higher concentrations gave yields that were too low to be measured.

2. Experiment

The principle of the experimental design is shown in the schematic of Fig. 3a. Reaction in the vapor film is detected by measuring the flow rate of product gases and conducting chemical analysis of the bulk liquid. For a simplified case where primarily noncondensable gases are produced and unreacted vapors of the bulk liquid are completely condensed, the measured flow rate is indicative of all gaseous products of the conversion process. In reality, condensable species can be produced and dissolve in the liquid pool, as is the case for EG [1]. These species are detected by GC/MS analysis of the bulk liquid. In the event of soluble products being formed, the gaseous species that pass through the flow meter would not represent the entire suite of products, which complicates the interpretation of the results. The present study concerns the overall performance of the conversion process with water dissolved in the liquid, and on inferring the reaction pathways to producing gaseous species. The term "product yield" is used to signify the gaseous species produced by reaction in the vapor film, with the understanding that this flow rate may not be indicative of all that is formed. The apparatus includes the capability to remove noncondensable gaseous species from the exhaust stream and to chemically analyze the bulk liquid.

Fig. 3b is a schematic of the design. A brief overview is given with more details provided in [1,3]. The design consists of three parts: (1) a glass containment vessel within which is mounted a horizontal tube held in place by vertical copper rods clamped at each end of the tube that pass through liquid-tight fittings screwed into the top metal flange cover; (2) a series of condensers and vapor traps that are sized to remove condensable gases from the gas stream; and (3) a data acquisition section that includes a digital flow meter (Omega #FMA-A2309, ± 0.1 SLM) to measure the gas flow rate, and a computer-controlled power supply to adjust heat input to the tube (Agilent #6681 A DC power supply, ± 0.0001 A). A capability is also included for liquid sampling.

Product gas species are identified by gas chromatography (GC) analysis (using a GOW-MAC Instruments series 600-TCD gas chromatograph (GC)), and a PC with LABView to control conditions and store flow rates and temperatures. GC analysis identifies primarily major and stable species in the product gas stream. Intermediates are not normally able to be detected. As a result, using information from GC analysis to infer reaction pathways provides information on global decomposition reaction pathways, rather than detailed kinetic mechanisms that involve intermediate species. Similarly, the product gas stream will only contain the stable species.

A schematic of the tube assembly on which the FIBOR is established is shown in Fig. 4a. The tube material is Inconel 600 (an iron/nickel/chromium alloy, from Microgroup # 600F10093X010SL) with dimensions of 2.38 mm OD, 1.85 mm ID and 79.4 mm long. The active boiling length is 60.4 mm owing to electrode clamps (not shown in Fig. 4a) attached to the ends (covering approximately 9.5 mm at each end). The tube diameter selected was smaller than previously used [1] as it allowed for a more stable film boiling configuration though with lower product yields.

Temperature is measured at four locations along the tube axis with 25 μm diameter thermocouples (Omega #KMQXL-010G-18, ± 1.0 K) positioned inside of the tube at the locations shown in Fig. 4a. A ceramic insert (Omega, ORX-132116) provides electrical insulation between the thermocouples and Inconel, and structural support to the tube which is heated close to its melting temperature (1686 K). More than four thermocouples could not be placed in this insert. In addition, temperature was measured by a thermocouple placed in the liquid and the average value over the duration of an experiment was recorded as the bulk liquid temperature (T_∞) from which the liquid subcooling, $T_{sat} - T_\infty$, was determined.

Fig. 4b shows temperature distributions during film boiling for three heat fluxes. The surface temperature is nearly constant over the length where the measurements are made, though there will be some reduction at the ends owing to axial conduction effects. A silicone sealant (Dow Corning, RTV 736) is used at the ends of the heater tube to prevent liquid penetration into the tube. It should be noted that there is expected to be a significant drop-off in temperature near the ends of the tube where the tube is clamped by the electrode mounts (i.e., the area between TC-1 and TC-4 to the lightly shaded zone).

Three surface conditions were examined: bare polished tube; nickel alloy coating; and platinum coating. The metal coatings served as catalysts to assess the potential for increasing product yields at lower surface temperatures compared to a bare tube. At the same time, the minimum film boiling temperature may increase with the surface roughness [7,11] associated with the catalyst. The catalyst coatings were applied by Catacel Corporation (Garretsville, Ohio) in a multistep procedure that included oxidation of the tube surface, application of an alumina (Al_2O_3) washcoat for adhesion followed by application of the metal catalyst by impregnation in the alumina layer. Further details on the catalyst application process are given in [2,3]. For the 2.38 mm O.D. tubes examined, the mass of Pt that was applied to the active boiling area (Fig. 4a) for the results reported here is 25.0 (± 0.1) mg, and for the Ni coating it is 15.3 (± 0.1) mg. Within the coating the weight fraction of Pt was 49% and for Ni it was 33%.

The liquid mixtures were prepared on a volumetric basis. Three concentrations were examined (volume percent EG/volume percent water): 100/0; 90/10; 80/20. Higher water concentrations resulted in product yields too low to measure accurately owing to dilution of the vapor film by steam (cf, Fig. 2). As the purpose here was to illustrate the potential for film boiling to affect chemical change of a miscible mixture, the three compositions selected were sufficient for that purpose.

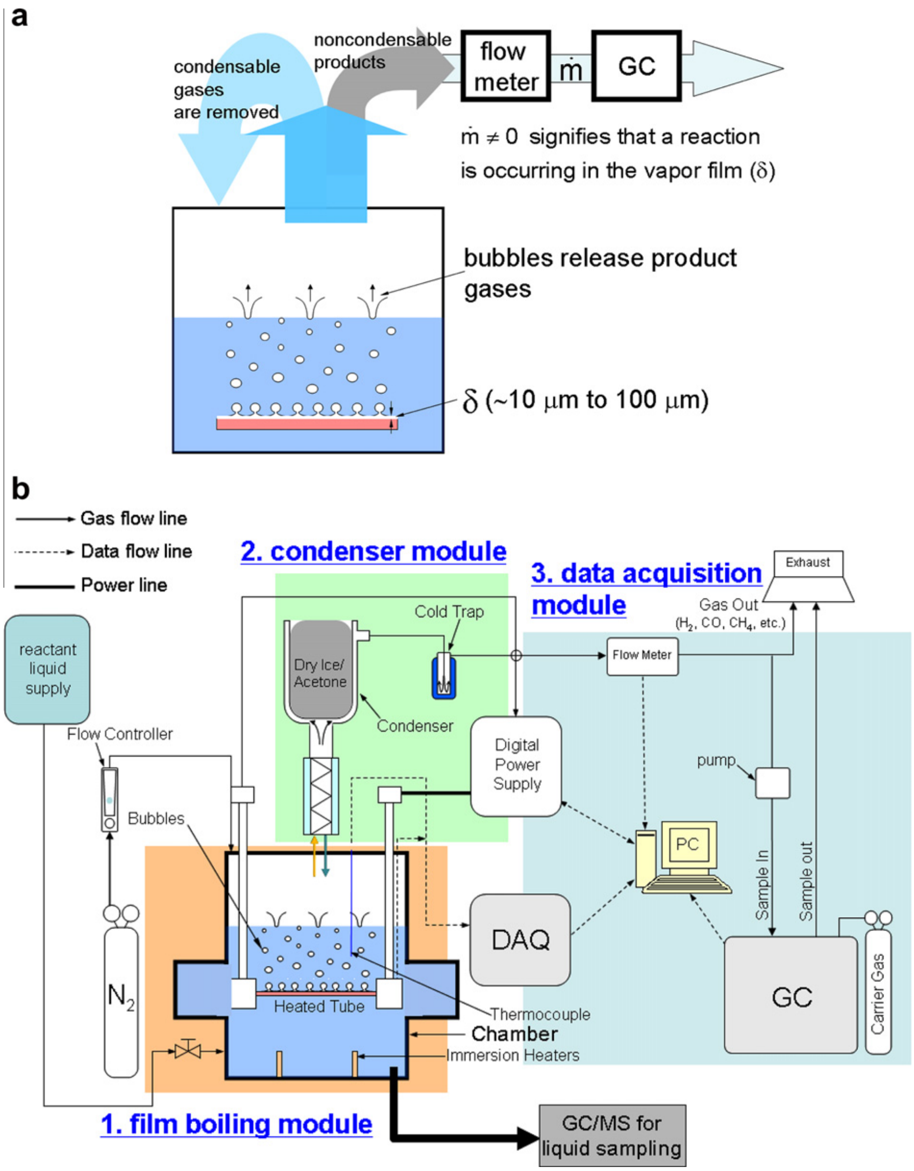

Fig. 3. (a) Schematic of gas flow paths in the experiment; (b) details of apparatus.

To achieve film boiling, a typical process would be to initially immerse the tube into the subcooled fluid and slowly heat the tube to transition the heat transfer regimes through the single phase and boiling regimes that culminate in film boiling. Once in the film boiling regime, the input power is adjusted to vary the surface temperature while the product gas flow rate is measured. This process worked well when using bare tubes for determining the boiling curve through the critical heat flux state.

The process of achieving film boiling for catalyst coated tubes must not allow the tube to come into contact with liquid, as doing so could deactivate the catalyst. Initially submerging the tube into the subcooled liquid and then raising the temperature of the submerged tube will not, therefore, work. There are also difficulties for bare tubes with this procedure because of the challenge of coordinating the approach to CHF with managing the attendant wall temperature excursion that could lead to burnout.

An alternative procedure was employed that involved a coordinated process of pre-heating the tube surface while it is initially positioned above the liquid pool, then slowly raising the liquid level to surround the preheated tube to achieve full immersion. Nitrogen gas was circulated above the liquid pool as a safety precaution to eliminate the potential for ignition of the vapors during the immersion process. Careful adjustment of the power to the tube is required to compensate for quenching the tube just as the liquid attempted to come in contact with the tube as the tube becomes submerged. Once in film boiling the nitrogen flow was turned off. This process proved effective for creating the film boiling regime, and it was also used for the bare tubes. The depth of submersion of the tube at the start of an experiment was fixed at approximately 4 cm in the experiments reported. Once in film boiling, GC measurements are made at several selected average tube temperatures to identify the species in the gas stream.

Each experimental condition was repeated at least twice. The results for the bare and catalyst-coated tubes were consistent between repetitions for the boiling curves (heat flux). However, product yields showed considerable differences between a new catalyst and one on which film boiling had already been developed. The differences are most likely due to degradation of the catalyst by the film boiling process that can result in cracks and delamination at the surface associated with power cycling when the power is terminated and the tube is allowed to cool back down to room temperature. More details and discussion of this effect are given in [3]. Some results showing the morphological changes that occur on a catalyst tube subjected to film boiling are discussed in Section 3.3. In the present study, results are presented primarily for what amount to surfaces that had not previously been subjected to film boiling.

In developing the variation of heat flux and product yield with average tube temperature, a staged power increase was employed. Each power setting was imposed for approximately two minutes before proceeding to a new power setting. This dwell time allowed steady state temperatures to be reached. Within each setting the outputs from the flow meter (Fig. 3) and current through the tube were recorded for later processing to determine an average product yield and heat flux. The energy input to the liquid was computed from the measured current (I) through the tube and the electrical resistance (R) of the tube as $Q = I^2R$ where $R = \frac{\rho(T_w)L}{A}$ and $\rho(T_w)$ is the temperature-dependent electrical resistivity of the tube material. For Inconel 600, ρ is determined by the following polynomial with the wall temperature (T_w) in Kelvin [12]

$$\rho(T_w) = 0.4763 + 5.27 \times 10^{-3}\,T_w - 1.95 \times 10^{-5}T_w^2 + 3.56 \times 10^{-8}\,T_w^3 - 3.23 \times 10^{-11}\,T_w^4 + 1.35 \times 10^{-14}\,T_w^5 - 1.89 \times 10^{-18}\,T_w^6$$

Since the tube area is $A = \pi\ D\ L$, the heat flux $q'' = q/A$ will be independent of L when the same length is used to compute q'' and R.

The temperature assigned to the heat flux was assumed to be the average of the four locations shown in Fig. 4a. This average will be different from the actual average temperature that would have been obtained were it possible to insert more thermocouples into the tubes, because of the expected drop-off of temperature at the end of the tube where the electrodes are attached due to conductive losses [1]. An additional consideration is the temperature drop in the radial direction, namely from the location of the thermocouple and the outside surface of the tube. A simple conduction model [3] was used to estimate these effects which showed that the cumulative correction would be less than 5K for the range of input powers examined.

3. Results

3.1. Boiling curves

Fig. 5a shows the variation of heat flux with surface temperature (averaged from the four measurements at the locations shown in Fig. 4a) for the liquids and catalysts examined. Table 1 lists the CHF, minimum film boiling temperature (T_m), bulk liquid temperature (T_∞) and subcooling ($T_{sat} - T_\infty$), where T_{sat} is the bubble point temperature (Fig. 2) at the bulk liquid composition and the indicated bulk composition (expressed as a volume percent). The nucleate boiling portion of the boiling curve is shown only for the polished tubes, as it was necessary to avoid any liquid/catalyst contact to prevent catalyst deactivation. The film boiling regime includes both bare and catalyst coated tubes. Since the experimental

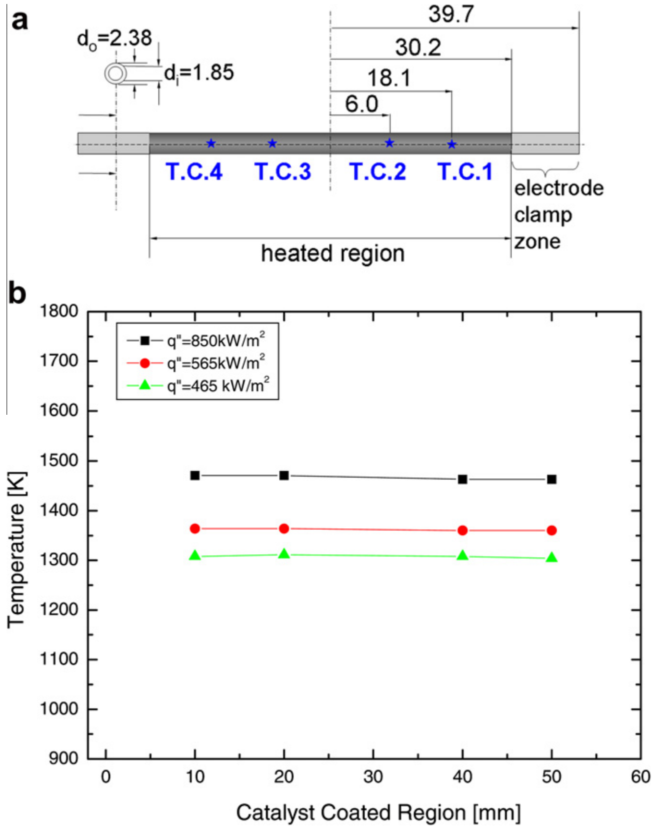

Fig. 4. (a) Schematic of tube assembly for film boiling showing locations of the thermocouples. The dimensions are in millimeters. Lightly shaded area of tube is in contact with electrode clamps and not exposed to reactant liquid. (b) Representative variation of surface temperature with distance along the tube for the locations in "a" at the three heat fluxes listed in the inset.

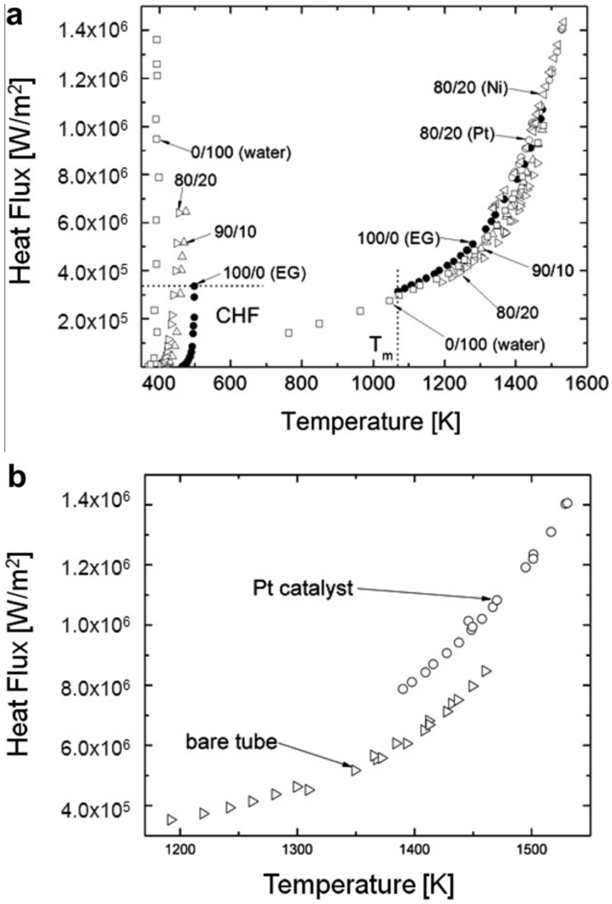

Fig. 5. (a) Boiling curves for ethylene glycol and the mixtures examined. Water data are included for reference. The nucleate boiling portion of the boiling curve for the catalyst-coated tubes was not measured to avoid liquid/surface contact. Dotted lines indicate minimum film boiling temperature (Tm) and CHF for pure ethylene glycol. (b) Data in the film boiling regime showing greater detail for an 80%EG/20%water mixture for a bare tube and a tube coated with a Pt catalyst (two trials; bare and 1st trial data are rescaled from figure 5a).

Table 1
CHF and minimum film boiling temperatures (T_m) for the specified fluids and surface conditions (subcooling ($T_{sat} - T_\infty$) is given in parenthesis).

Mixture (%EG/%H_2O)	Surface condition	CHF (W/m^2)	T_m (K)	T_∞ (K)
100/0	Bare	0.335×10^6	1071	440 (30)
90/10	Bare	0.647×10^6	1221	407 (8)
80/20	Bare	0.641×10^6	1192	397 (0)
80/20	Pt catalyst	-	1390	393 (2)
80/20	Ni catalyst	-	1336	393 (2)
0/100	Bare	1.36×10^6	763	373 (1)

procedure controls the input power, the transition boiling regime of the boiling curve is not accessible.

With dilution by water, the nucleate boiling heat flux increases substantially with water addition. In the film boiling regime, adding water to EG lowers the film boiling heat flux compared to EG, though the influence is not as significant as in the nucleate boiling portion. In film boiling the gas properties (e.g., gas thermal conductivity) mainly determine the heat flux as heat is transferred across a vapor layer surrounding the tube. In nucleate boiling the complex processes of nucleation, growth, bubble detachment and liquid motion are more strongly dependent on both gas and liquid properties (e.g., liquid surface tension, viscosity and specific heat, etc. [13]).

The influence of composition on the CHF for the liquids examined showed that diluting EG with water substantially increased the CHF for the 90%EG/10%water and 80%EG/20%water mixtures compared to EG. Viewed in terms of liquid properties, the influence of surface tension and heat of vaporization on mixture CHF appears to be strongest [13]. Interestingly, this trend is different from that noted previously for mixtures of EG and water [14] where the CHF of EG was found to be nearly the same as EG/water mixtures. The heater geometry employed was different–a flat plate compared to the tube configuration examined here. The different geometries may explain the trends. For the tube, a counterflow effect in nucleate boiling is probably not as substantial as for a flat plate confined by walls. For a tube, fresh liquid can be drawn more easily toward the tube from the lower hemisphere as bubbles depart from the top, thereby keeping the composition at the liquid/vapor interface more like the initially prepared composition. Nonetheless, we find the CHF's for pure components to be consistent with values reported in literature for EG [1] and water [13].

In the film boiling regime, Fig. 5a shows that higher heat fluxes in the 80%EG/20% water mixtures are required to support the vapor film for the catalyst tube compared to a polished bare tube. This trend is more clearly illustrated in Fig. 5b which shows the data of Fig. 5a on an expanded scale. The higher fluxes for the Pt catalyst-coated tube suggests a greater endothermicity to the decomposition kinetics and a greater energy requirement to maintain the vapor film compared to film boiling on the bare tube. The catalytic conversion kinetics that would explain this trend have not yet been developed.

The lowest temperatures shown in Fig. 5 in the film boiling regime represent the minimum film boiling temperature (or Leidenfrost point). Values are listed in Table 1 where it is evident that the influence of water concentration on T_m is not monotonic. When $T_w < T_m$ the films destabilize and the reaction process ceases. For example, below about 1192 K for film boiling on a bare tube of an 80%EG/20%water mixture (Fig. 5b), the vapor film collapsed. T_m was found to be higher for the tubes with a catalyst than the bare tubes for the same liquid composition, suggesting a tendency for destabilization of the film due to surface roughness effects at high temperatures [7,11]. The results also show that the film boiling heat fluxes are not substantially influenced by the catalyst type (Pt or Ni) for a given T_w.

3.2. Product yields

The measured gas flow rate per unit area (flux of product yield) downstream of the condenser and vapor traps (Fig. 3) is shown in Fig. 6 for pure ethylene glycol on a polished tube. The dotted lines are polynomial fits of the raw data. Because the condensable gases have been removed, the flow rate is indicative of species produced by the decomposition reaction in the vapor film. The temperature in Fig. 6 is an average of the four thermocouples over the central region of the tube (Fig. 4a) while the flux is based on the full tube area between the clamps. As such, the measured fluxes of product yields in Fig. 6 will be shifted slightly to lower average surface temperatures.

Also shown in Fig. 6 are data from Choi et al. [1] for a 4.76 mm O.D. tube for comparison. The product yield fluxes for the larger diameter tube are considerably higher than the smaller tubes of the present study. During prolonged film boiling of EG on the 2.38 mm O.D. tubes employed in the present study, the bulk liquid temperature decreased over time. This effect was previously shown (for larger tubes [1]) to be the result of species formed during the EG decomposition process that were soluble in the bulk liquid. The influence of product species solubility in the reactant liquid deserves further study.

The undetectable yield below 1100 K is a manifestation of the thermal structure of the vapor film (Fig. 1b) in which the temperature changes from T_w at $y = 0$ (see Fig. 1b) to $T = T_r$ ($>T_{sat}$) at $y = \delta_r$. If the reaction layer bounded by T_r and T_w is too small, the yield will not be high enough to be detected, even though EG is in fact decomposing at lower temperatures. This situation is evidently the case here.

Below about 1100 K in Fig. 6 (which is the temperature T_r in Fig. 1b), the EG yield is below the detectable range for the flow meter. This does not mean, however, that EG decomposition will not occur at lower temperatures. Indeed, several studies have reported on the pyrolysis of heavy glycols (e.g., glycerine) at temperatures below 700 K [15]. For a decomposition process governed by Arrhenius kinetics, the conversion rate k will be such that $k \propto e^{-\frac{E}{RT}}$. The conversion rate will therefore be nonzero at virtually any temperature. However, there are practical limits on instrumentation precision to detect the product gas flow rate, which appear to be

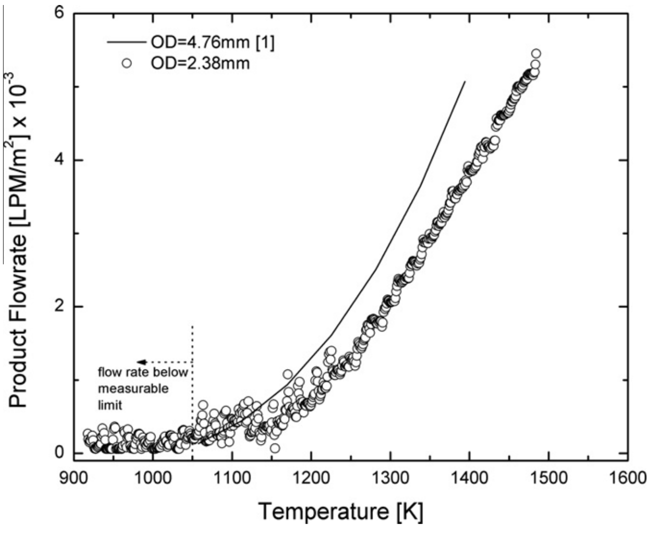

Fig. 6. Variation of measured product gas flow rates with average surface temperature for ethylene glycol. Line is average of data from [1] for a larger tube (4.76 mm O.D.). Lower film boiling limits are indicated for the 80%EG/20% water mixtures for the catalyst surfaces.

reached at around 1100 K for the instrumentation employed in the present study.

The residence time of reactant molecules as they are transported through the high temperature zone of the vapor film (e.g., by buoyancy in the vapor film or by a carrier gas in a packed bed reactor) determines the reactant decomposition rate. Conventional reactor designs (e.g., the tubular or packed bed reactor) achieve high yields at low temperatures by promoting long residence times (order of seconds or larger). By contrast, for pool film boiling of a horizontal tube in a gravitational field the residence time is not a control variable but is instead determined by the mechanism that moves gases in the vapor film around the tube, which for the present study is buoyancy. Residence times on the order of tens of milliseconds are estimated for this situation [5]. To compensate, higher average gas temperatures are necessary for conversion by film boiling to occur at measurable rates within the film. Alternative surface geometries and orientations that would seek to increase the residence time for supporting film boiling could alleviate this concern.

Fig. 7 summarizes the data obtained on product flow rates for all of the systems investigated here. The variation of product gas flow rate with average tube surface temperature is shown. Data for bare polished tubes (i.e., tubes with no catalysts) and tubes with the metal coatings examined are shown. Several trends are immediately obvious.

Increasing the water concentration reduces the product yields. This fact reflects the significant depletion in the vapor film of EG owing to the phase equilibrium behavior of the mixture (Fig. 2). For example, at water dilutions greater than 20% (i.e., 80% EG in the liquid), the EG concentration relative to water in the film is less than 10% by Fig. 2. The product yields are correspondingly very low as shown in Fig. 7. Additionally, with a catalyst coating the tube, chemical reactivity is enhanced significantly. For example, product flow rates for an 80%EG/20% water mixture are three to four times higher for the coated tubes compared to bare polished tubes at overlapping temperatures for this same mixture.

The product yields for the coated tubes are considerably higher at the same average tube temperature than for the bare tube, indicating significant catalytic activity. The differences appear to decrease as T_w increases. This trend is consistent with the fact that catalytic decomposition is largely a surface phenomenon while thermal decomposition (i.e., conversion without a catalyst present) is a more volumetric process as it occurs over a temperature range (i.e., between T_r and T_w in Fig. 1b). As T_w increases, δ_r (Fig. 1b) will also increase since T_{sat} is fixed.

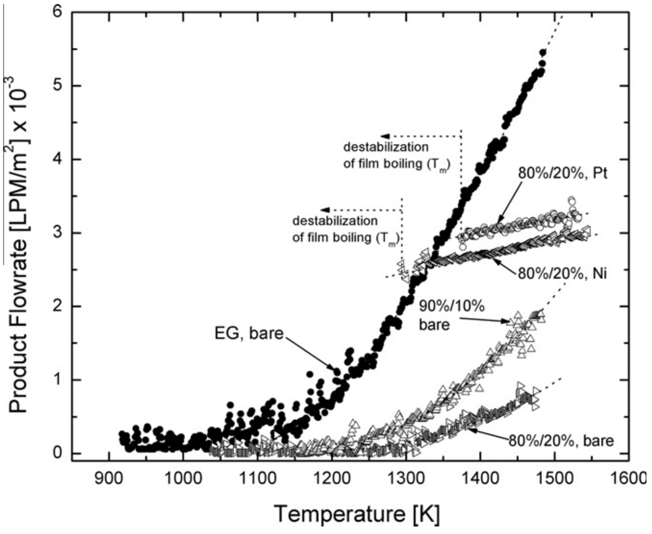

Fig. 7. Variation of product gas flow rate with average surface temperature for the mixtures examined on a bare tube, and Pt and Ni coated tubes. EG data are from Fig. 6. Dotted lines are included to show trends. Limits for collapse of film boiling are indicated for 80%EG/20% water mixtures with Pt and Ni catalyst coatings.

The trajectories of product yields with T_w for the bare and catalytic tubes converge as shown in Fig. 7 suggesting that thermal decomposition will become controlling at very high temperatures. The limit on the upper value of T_w is dictated by structural considerations of the tube material. The highest temperature that could safely be imposed without serious damage to the tube occurring was $T_w \sim 1550$ K.

Below 1336 K for the Ni catalyst and 1390 K for the Pt catalyst in 80%EG/20% water mixtures, the vapor film destabilized, film boiling collapsed, T_w dropped precipitously and the conversion process abruptly ceased. Here, evidently[4] $T_r \sim T_m$. The product yields for the bare tubes show a much more gradual reduction with T_w because the vapor film exists on the bare tubes at temperatures where the yields are at the limit that they can be accurately measured. For the catalyst tubes, the comparatively high T_m (Table 1) leads to a more abrupt termination in the conversion process because of the vapor film collapsing at temperatures where the yields can still be measured accurately.

3.3. Product gases

GC analysis was performed for the two mixtures investigated. Table 2 shows representative results and Fig. 8 a representative GC trace for an 80%EG/20% water mixture at $T_w = 1373$ K (the figure caption gives the relative proportions of the species). For both the bare and coated tubes the same product species are found. Film boiling for the catalyst-coated tubes ranged over surface temperatures between about 1300 K and 1450 K (Fig. 7) which constrained GC sampling to a temperature range of only about 200 K. The tiny trace of air (N_2 and O_2) indicated by the dotted box in Fig. 8 is due to a small amount of atmospheric air being entrained in the gas line downstream of the flow meter, yet before entering the GC.

For the bare tube, Table 2 shows that thermal decomposition of the 90%EG/10%water and the 80%EG/20% water mixtures result in little change of the product yields with water concentration for the major species formed. By contrast, comparing results for a given T_w, the reaction process is significantly influenced by the Pt catalyst, with now H_2: CO ~ 3 for the 80%EG/20% concentration compared to the bare tube as shown in Table 2. The H_2 yield increases by over 45% with a Pt coating compared to film boiling on a bare tube, and the CO yield drops by approximately the same amount.

The concentration of CO_2 was found to be low (<1%) for the bare tube but was significantly higher for the Pt-coated tube (7% and 8%). The product gases formed on the bare tube contained approximately 10% CH_4 which dropped by almost an order of magnitude (to about 1%) on the catalyst. Ethane and ethylene were also found at about 2.5% on the bare tube which dropped by a factor of ten for catalytic decomposition.

As remarked earlier, GC analyses of the product gases identifies stable species, and from these species global mechanisms may be inferred. The thermal decomposition reactions will occur within the vapor layer from $y = 0$ to $y = \delta_r$ (as schematically shown in Fig. 1b). For the catalyst tubes surface reactions also. For the Pt and Ni coated tubes, both reaction processes – thermal and catalytic decomposition – appear to work together to produce significant enhancement of yield as shown in Fig. 7.

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[4] There does not appear to be a known relationship between T_r and T_m. The product yields will depend on the residence time of reactant molecules as they flow around the tube surface, which in turn influences T_r.

Table 2
Product gas composition (mole percent) and tube conditions for the specified fluids and surface conditions at the indicated temperatures.

Mixture (%EG/%H_2O)	Surface condition	T_w (K)	H_2 (%)	CO (%)	CH_4 (%)	CO_2 (%)	C_2H_2 (%)	C_2H_4 (%)
90/10	Bare	1473	43.7	40.3	11.1	0.7	2.4	1.8
80/20	Bare	1473	44.8	40	9.4	0.9	2.6	2.2
80/20	Pt catalyst	1373	68.7	22.9	1.1	6.8	0.3	0.1
80/20	Pt catalyst	1473	67.8	21.7	1.6	8.3	0.4	0.2

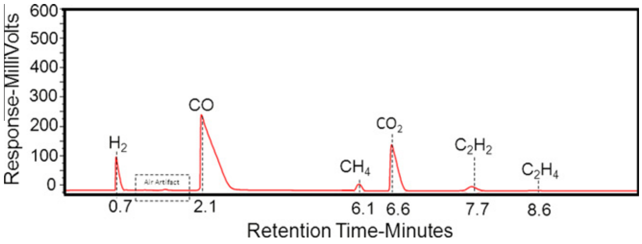

Fig. 8. GC trace for an 80%EG/20%water mixture for film boiling at an average tube surface temperature of 1373K with the following products and mole percents: H_2 (68.7%), CO (22.9%), CH_4 (1.1%), CO_2 (6.8%), C_2H_2 (0.3%), and C_2H_4 (0.1%).

The global decomposition reaction of EG would be

$$C_2H_4(OH)_2 \rightarrow 2CO + 3H_2$$

Since some methane is produced it could be formed by

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

With steam in the vapor film as for an aqueous mixture, the overall steam reforming reaction

$$C_2H_4(OH)_2 + 2H_2O \rightarrow 2CO_2 + 5H_2$$

is viable. With CO_2 also found in the product stream it could react with H_2 as

$$CO_2 + H_2 \rightarrow CO + H_2O$$

Along with these gas phase reactions are those that would lead to formation of solid deposits (i.e., carbon or coke) on the surface. The formation of acetylene (C_2H_2) and ethylene (C_2H_4) as indicated in Fig. 8 forecast carbon deposits on the tube with prolonged operation. Previous studies of film boiling of various pure organic liquids noted formation of a solid layer that was considered to be carbon-based [1,4,16–20]. Formation of a solid layer was observed for pure EG and a 90%EG/10%water mixture, but not for 80%EG/20%water mixtures.

If the layer is carbonaceous, possible global reactions for its formation could include

$$2CO \rightarrow C_{(s)} + CO_2$$

$$CH_4 \rightarrow C_{(s)} + 2H_2$$

$$CO + H_2 \rightarrow C_{(s)} + H_2O$$

and/or

$$CO_2 + 2H_2 \rightarrow C_{(s)} + 2H_2O$$

With steam introduced in the vapor film, carbon formation could be suppressed by the reaction

$$C_{(s)} + H_2O \rightarrow CO + H_2$$

and a surface layer may not form. How much steam is needed to influence the decomposition kinetics that lead to carbon or coke formation is a matter of speculation. For the 90%EG/10%water mixture for which a noticeable dark coating formed, the water concentration in the vapor film is anticipated to be rather high: 70% relative to EG (cf, Fig. 2). Yet, a layer is still formed. For an 80%EG/20%water liquid mixture the water concentration (relative to EG) in the vapor film would now be approximately 90% based on

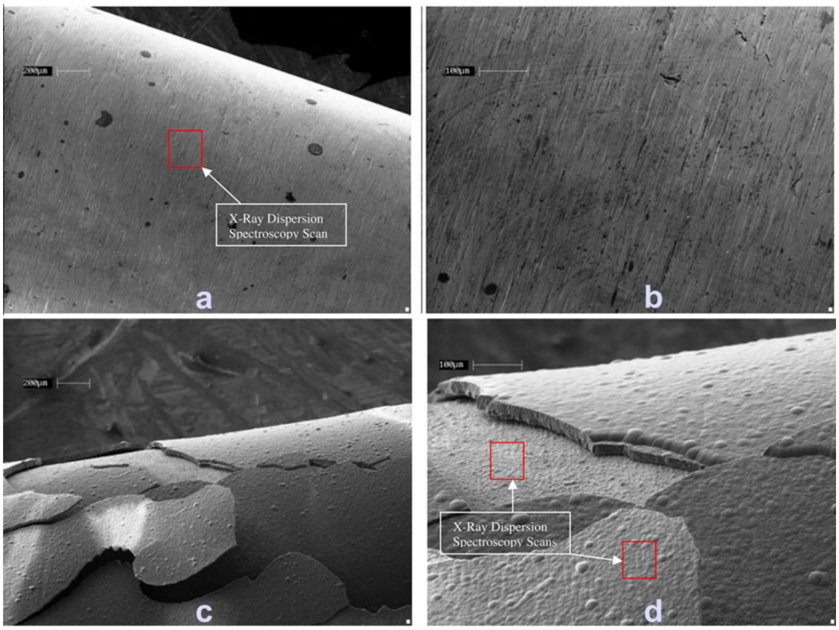

Fig. 9. SEM images of a bare tube (a) at 100X and (b) at 300X, for a tube before film boiling of a 90%EG/10%water mixture. SEM images after film boiling (c) at 100X and (d) at 300X. The boxes show where X-Ray dispersion spectroscopy scans were taken for Fig. 11.

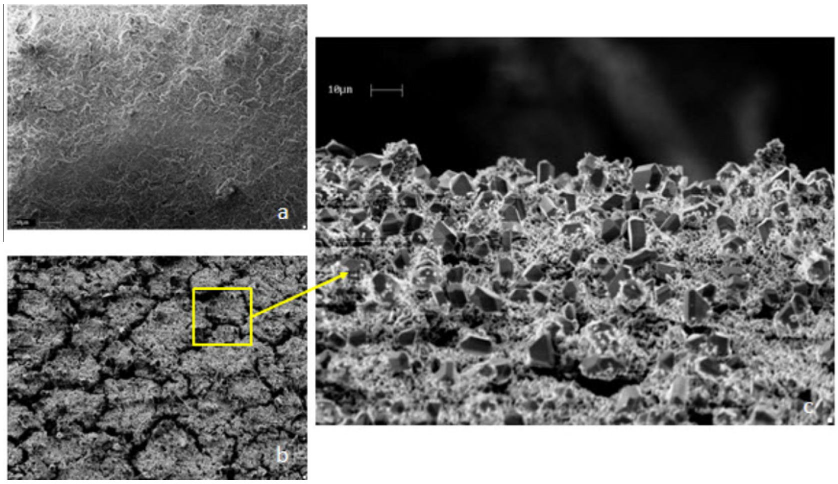

Fig. 10. SEM images of Ni catalyst surface before (a, b) and after (c) film boiling of an 80%EG/20% water mixture at 300X and 600X, respectively. (c) is an enlarged image of the Ni catalyst surface at 1800X.

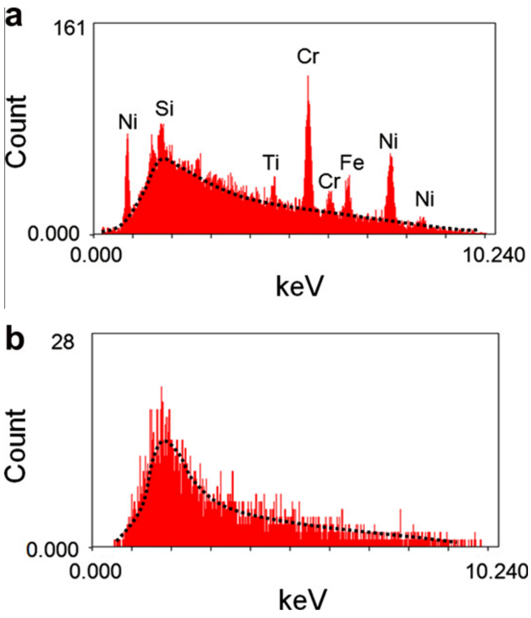

Fig. 11. X-ray diffraction scans of a bare Inconel tube (a) and a bare tube after film boiling in ethylene glycol (b). The tube after film boiling was coated with a black material (Fig. 10) that (b) indicates is non-metallic. The dotted line shows the baseline.

Fig. 2. This concentration is now evidently high enough that a layer is not observed after film boiling.

The morphology of the surface of a bare (polished) tube before and after film boiling is shown in the scanning electron micrograph (SEM) images of Fig. 9 for a 90%EG/10%water mixture. The surface structure of a tube before film boiling is shown in Fig. 9a and b at a magnification of 100X and 300X, respectively. There is no evidence of surface imperfections at this scale. After film boiling on the bare surface, Fig. 9c and d show the structure of the layer that has formed. Significant delamination of the deposit is evident.

Fig. 10 shows the structure of a tube coated with a Ni catalyst before (Fig. 10a) and after (Fig. 10b) film boiling of an 80%EG/20%water mixture at a magnification of 600X. Fig. 10c is a magnified image of Fig. 10b (1600X). The SEMs show a changing catalyst structure in film boiling. Cracks are visible in the surface layer and particles of a crystal-like structure appear to have formed at the surface (Fig. 10c). These results suggest that while catalysts for film boiling may enhance product yields at a given temperature (cf, Fig. 7), the integrity of the catalyst coating can degrade with sustained film boiling.

Some limited X-ray dispersion spectroscopy analysis was used to identify the chemical elements of the film boiling surface. Fig. 11a shows a bare surface with elements identified over the peaks (above a background (dotted line)) that are consistent with an Inconel Alloy. After film boiling of a 90%EG/10%water mixture where a layer was formed (Fig. 11b) the scans reveal only that the deposit is apparently not metallic, in keeping with the belief that the deposit could be carbonaceous.

4. Conclusions

This study has shown the potential of film boiling to convert an aqueous ethylene glycol mixture to various products. The conclusions are the following.

1. The predominant product for EG decomposition is synthesis gas.
2. A non-metallic deposit forms on the heater surface for pure EG and a 90% (EG)/10% (H_2O) reactant mixture. At 20% water dilution in the liquid no deposits were found.
3. Increasing the amount of water in the liquid lowers product yields because of enrichment of steam in the vapor film and depletion of EG in the film owing to the phase equilibrium behavior of the mixture.
4. Catalytic conversion of the aqueous mixtures results in significantly higher product yields compared to conversion on a bare surface for the same average tube temperature and liquid composition. The catalytic and decomposition flow rates appear to converge at high surface temperatures as the thermal affect for decomposition overrides catalytic processes, perhaps due to degradation of the catalyst at high tube temperatures.
5. The decomposition products are significantly enriched with hydrogen for catalytic conversion (H_2: CO $\sim$ 3) compared to thermal decomposition (H_2: CO $\sim$ 1). Methane production is significantly lower for catalytic conversion ($\sim$1% in the product stream) compared to thermal decomposition ($\sim$10% in the stream), while the concentration of CO shows the opposite trend. Small traces of acetylene (C_2H_2) and ethylene (C_2H_4) are detected for both means of conversion (catalytic and thermal) with slightly higher amounts detected for thermal decomposition.

6. Platinum exhibits slightly better performance than nickel as a catalyst in terms of overall product yield and resistance to deactivation. Nickel, however, will be more attractive at larger scales due to its comparatively lower cost.
7. The minimum film boiling temperature was close to the tube temperature limit where decomposition could just be detected. The coated tubes had significantly higher Leidenfrost temperatures than the bare tubes.

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