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Rapid Screening of Fluids for Chemical Stability in Organic Rankine Cycle Applications

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While the Carnot cycle is the basic idealized thermodynamic cycle for energy transfer, it is generally impractical and uneconomical to implement. Although less thermodynamically efficient than the Carnot cycle, the Rankine cycle (and heat engines based upon it) is practical and adaptable. Typically, water is used as the working fluid in this cycle. A difficulty that arises with the use of water is the need to superheat the water to prevent turbine blade erosion. Organic working fluids, on the other hand, can be used at lower temperatures and do not require superheating. This results in a practical increase in efficiency over the use of the cycle with water as the working fluid. In these organic Rankine cycle (ORC) applications, the choice of working fluid is critical since the fluid must have not only thermophysical properties that match the application but also adequate chemical stability at the desired working temperature. In this paper, we present the application of simple and relatively rapid ampule testing techniques by which the chemical stability of potential working fluids may be assessed. The method allows the determination of the decomposition reaction rate constant of simple fluids at the temperature and pressure of interest. The fluids studied were pentanes, which are being considered for application in parabolic solar collectors. Results show that the thermal stability decreases in the following order: *n*-pentane > 2-methylbutane > 2,2-dimethylpropane and benzene ≫ toluene.

Introduction

The theoretical Rankine thermodynamic cycle is used in numerous applications to generate electrical power. Consisting of a heat engine with a vapor power cycle, it is the practical engineering alternative to the idealized Carnot cycle. It consists of (1) an isentropic expansion through a turbine (or other work-extracting machine), followed by (2) isobaric heat transfer (cooling) in a condenser, followed by (3) isentropic compression in a pump, followed by (4) an isobaric heat transfer (heating) in a boiler. The cycle is depicted schematically in Figure 1. In practical Rankine cycles, steps 1and 3 are not strictly isentropic. The cycle is usually implemented with water as the working fluid and forms the basis of familiar electrical power plants that operate worldwide. A disadvantage of using water as the working fluid is the need to superheat the steam to approximately 600 °C to prevent condensation during the expansion (step 1 above), a problem that results directly from the thermophysical properties of water.[1] Such condensation is problematic because it can lead to erosion of the turbine blades. The choice of alternative working fluids can circumvent the superheating requirement, especially in applications that can be operated at lower temperatures, or that have a lower heat resource temperature (from 100 to 400 °C). In these situations, an organic working fluid offers advantages in efficiency since in many cases superheating is unnecessary. These cycles are called organic Rankine cycles (ORC). The
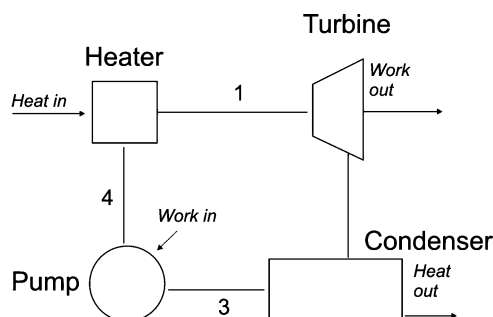

Figure 1. A schematic depiction of the organic rankine cycle.

working fluids for ORCs are often called "heavy" fluids, as a result of the comparison with the lower relative molecular mass (RMM) of water. Another advantage worth noting is that the turbine of engines built on the basis of ORCs typically requires only a single-stage expander, resulting in a simpler, more economical machine in terms of capital costs and maintenance.

The lower operating temperatures of the ORC are ideally suited to waste heat recovery (from industrial processes) and to geothermal and solar electrical energy generation.[2,3] As applied to waste heat recovery, ORC engines can produce electrical power continuously with no interference to the primary process, and thus decrease fossil fuel combustion and CO_2 emissions.[2] For solar electrical generation with parabolic trough collector technology, ORC engines can form the basis of distributed modular power plants in the 500 to 1500 kW range. This has the potential to offer new applications to both ORC engines and solar power generation. The key to the successful operation of this combination of technologies rests in the appropriate choice of a working fluid for the ORC engine. The requirements for ORC working fluids are[4] (i) acceptable cycle and turbine

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efficiency, (ii) noncorrosivity, (iii) low cost, and (iv) high thermal stability.

The cycle and turbine efficiency ratings of a working fluid are related to temperature levels and differences and thermophysical property considerations, primarily critical constants, heat capacities, and transport properties. The requirement of low corrosivity is obvious, although it must be borne in mind that the corrosivity of a fluid can change with temperature and pressure. The economics of fluid selection is also an important consideration and is related directly to the thermal stability. The initial investment for the working fluid will be depreciated over some years. Thus, the fluid must have a high thermal stability for the ORC to be economical as a whole. It is therefore a critical step in the design of ORC engines to explicitly consider working fluid stability in a quantitative way. The working fluid must have sufficient stability to provide the desired lifetime, and the nature of the decomposition products that may form over time or in upset conditions must be understood. In this respect, designers must be aware of how departures from design conditions can produce corrosive products or sludge-forming foulants.

In this work, our primary concern was the applicability of pentanes as ORC working fluids for parabolic trough solar energy applications. In this context, it was critical to assess the thermal stability of a fluid at 315 °C and 4.1 MPa, typical operating conditions for such a collector. With this state point in mind, we also sought to address departures from the design conditions, especially large departures in pressure, since this variable can be much more difficult to control. There is a rich literature that deals with the decomposition of hydrocarbons and other organic fluids, many of which are highly complex.[5–7] Much of this work was done for fuels and propellants,[8–22] while some are more relevant to the specific ORC working fluids that are currently of interest.[1,23–30] This literature provides guidance on both experimental approaches and what may be expected in terms of results. There are, however, no available measurements that can address the decomposition of even these simple fluids under the conditions desired for ORC working cycles.

Theory

The most fundamental quantitative measure of working fluid stability is the decomposition reaction rate constant. If we assume that the decomposition of the fluid follows a first-order rate law, we can write

$$\text{Rate} = \text{d}[A]/\text{d}t = -k[A] \quad (1)$$

where [A] is the concentration of the organic working fluid, t is the time, and k is the first-order rate constant.[31] In the case of the decomposition of a single-component working fluid, the assumption of a first-order rate law is a useful initial approximation. In many cases, the thermal decomposition of a single organic working fluid by a free radical mechanism can be considered an elementary reaction.[31] One must keep in mind that decomposition products may themselves undergo subsequent thermal decomposition, thus complicating the elementary model. It is nevertheless useful to think in terms of a global decomposition reaction rate constant, initially assumed to be first-order.

One can check the validity of this assumption experimentally by examining [A] as a function of time. Thus,

if we plot ln[A] against t, we should obtain a straight line under first-order conditions. Moreover, we can define the half-life of the reaction as

$$t_{1/2} = \ln 2/k \quad (2)$$

where $t_{1/2}$ is the half-life, the time required for half of the initial quantity of A to decompose. Since, for a first-order reaction, the time for half of the initial concentration of fluid to react is independent of concentration, first and subsequent half-lives will show the same reaction rate constant. This behavior will be apparent on the plot of ln[A] against t. Note that this is not the case for reaction orders other than one, where $t_{1/2}$ will show some concentration dependence. In the case where the rate constant is determined from the increase in products, the half-life is more accurately described as the time interval required for the quantity of products to increase by a factor of 2. We note that these quantities are fundamental physical parameters that describe the chemistry; the use of half-lives in no way implies that it is possible to operate an ORC machine if significant working fluid decomposition occurs. Indeed, the goal here is to avoid operation in these regimes.

The usefulness of the first-order reaction rate constant in assessing the suitability of a working fluid is inherent in its fundamental nature. It can be used as a predictive tool to extrapolate an approximation of the long-term decomposition potential of a working fluid. While appreciable uncertainties in extrapolated data are to be expected for long-term predictions, the nature of a first-order rate constant establishes that the fluid decomposition rate measured at short times will be the same as that for long reaction times. Extrapolation is the only practical way to avoid extremely long-term experimental assessments (upward of 5 years) of fluid stability. Moreover, when combined with Arrhenius parameters (the pre-exponential factor and the activation energy), this approach can be used to predict the reaction rate constant at different temperatures. These Arrhenius parameters can be experimental or derived from kinetic theory. In either case, the approach provides a sound, defensible foundation upon which to base a process design.

Experimental Section

Chemicals. Normal pentane, 2-methylbutane, 2,2-dimethylpropane, toluene, and benzene were obtained from commercial suppliers. All fluids were used as received with the exception of n-pentane, which was purified by preparative-scale gas chromatography (1 m long, 1.27 cm diameter column packed with 60/80 mesh chromosorb W coated to 15% coverage with 5% phenyl polydimethyl siloxane; pump injection into a flash vaporizer; thermal conductivity detection). The purity of the fluids used for this work was determined by gas chromatographic analysis with flame ionization detection and was found to be 99.66 ± 0.06% for purified n-pentane, 98.58 ± 0.02% for 2-methylbutane, 99.89 ± 0.06% for 2,2-dimethylpropane, 99.83 ± 0.01% for toluene, and 99.98 ± 0.01% for benzene. All uncertainties herein are reported as one standard deviation ($k = 1$).[32]

Apparatus. The simple apparatus developed to make the decomposition kinetics measurements is shown in Figure 2. This apparatus has been described previously,
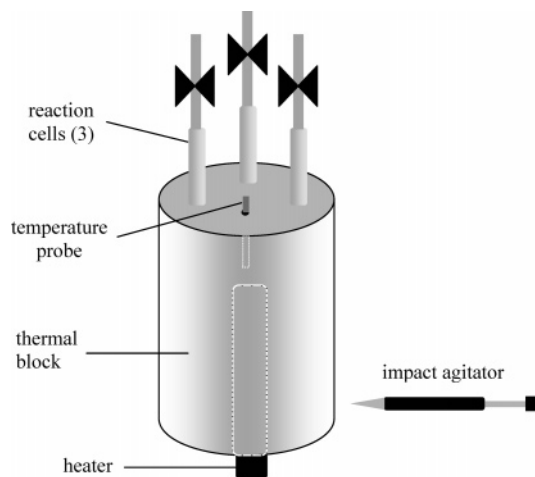
Figure 2. Apparatus used to thermally decompose organic fluids.

so only a brief summary will be provided here.[8] The apparatus consists of a 304L (AISI designation) stainless steel thermal block that is heated to the desired experimental temperature. In the work reported here, that temperature was 315 °C. Stainless steel was chosen for the block because of its favorable mechanical and corrosion properties at high temperature. The block is supported in an insulated box with carbon rods, which were chosen for low thermal conductivity. The temperature is maintained and controlled by a PID controller to within ±0.1 °C, in response to a platinum resistance sensor embedded in the thermal block and sealed with ceramic adhesive. The cells consist of 6.4 cm lengths of ultrahigh pressure 316L stainless steel tubing (0.64 cm external diameter, 0.18 cm internal diameter) that are sealed on one end with a brazed 316L stainless steel plug. Each cell is connected to a high-pressure valve at the other end with a short length of 0.16 cm diameter 316 stainless steel tubing with an internal diameter of 0.02 cm. Each cell and valve is capable of withstanding a pressure in excess of 105 MPa at the desired temperature. Although not used in the measurements reported here, an impact agitator is available as part of the apparatus for use when a heterogeneous catalyst is employed.

The internal volume of each cell (including the short length of connecting tubing, and the small dead volume of the valve) was determined by gravimetric gasometry with carbon dioxide as the fluid. This procedure consisted of filling a weighed, evacuated cell with carbon dioxide to a predetermined pressure (20.68 MPa) while the cell was maintained at a constant temperature. The cell was then disconnected from the manifold and weighed again. The increase in mass allowed calculation of the cell volume through a precise equation of state for the density of carbon dioxide.[33] Cell volumes were measured three times and averaged to yield 0.374 ± 0.001, 0.385 ± 0.003, and 0.447 ± 0.002 cm^3 for the three vessels.

The cell-filling procedure was a critical step since we desired to mimic the conditions in a parabolic solar trough. A computer program was developed (based on equations of state for each of the potential working fluids[34]) that provided the necessary fluid mass to achieve a selected pressure at the desired temperature. This program allowed us to determine the target mass that had to be added to the evacuated cell, given the cell volume as an input, to achieve a nominal 4.1 MPa

at 315 °C, typical operating conditions for parabolic trough solar energy applications. Note that in some experiments, the quantity of fluid added to the cells was intentionally varied to give a large range in resultant pressures.

Due to the volatile nature of the fluids studied, syringes, cells, and fluids were cooled to 7 °C prior to vessel filling. The filling procedure was the same for all of the liquid fluids, wherein the desired mass of fluid was added to the cell with a syringe equipped with an ultrafine needle. The valve was then affixed to the cell and sealed. In the case of 2,2-dimethylpropane, which is a gas at room temperature, the cells were filled by transferring the desired mass of 2,2-dimethylpropane into the chilled (−196 °C), evacuated cells with a gas manifold. Typical sample quantities for all fluids ranged from 0.02 to 0.30 g, varying to accommodate the different cell volumes.

The cells were loaded, weighed, and sealed quickly to minimize mass fluctuations from the evaporating fluid and from condensation of atmospheric water on the chilled cell exterior. The filled cell was then chilled in liquid nitrogen (to freeze the organic fluid) and subsequently evacuated to 10 Pa through the valve to eliminate air from the cell. This was important because any air present in the cell would react with the organic working fluid to produce oxidation products. Moreover, the equation-of-state volume calculation is predicated upon only the organic fluid being present in the cell. The valve was then closed and the cell warmed to room temperature, at which time the cell mass was recorded. Fluid mass was determined by mass difference and had a typical uncertainty of ±0.0004 g. Cells so loaded were then placed (in groups of three cells, to obtain three replicate measurements) into the thermal block and covered with glass wool insulation. This ensured that the entire cell would be at the experimental temperature for the desired reaction time. Fluid reflux inside the cells was minimized by ensuring that the entire length of the cell, transfer line, and most of the valve were located in the hot zone. The initial time was set and recorded as each vessel was inserted into the heating block.

The vessels were maintained at the reaction temperature for a specified period of time ranging from 40 h to 15 days. After the desired time period, the vessels were removed from the thermal block and quenched by cooling the vessels to 7 °C. The cells were weighed to ensure that no leakage had occurred during the course of the experiment. Measurements at multiple reaction times provided the data input for the first-order expression, eq 1.

The uncertainty in the time measurement was ±1 s. The uncertainty in the temperature measurement was ±0.5 °C. For the first 2−3 min of each measurement, after the cells had been inserted into the thermal block, the temperature was observed to drop by approximately 5 °C before recovery. Since this departure on initial heat-up of the samples is far smaller than the typical experimental times, it is not considered significant.

A blank experiment was performed to investigate any possible artifacts introduced in the experiment such as residual solvent in the cell or possible catalytic behavior of the cell materials. The cells were loaded and evacuated as described above and then maintained at room temperature for 65 h. The liquid sample was then removed and analyzed in the same manner as the samples that had been exposed to elevated temperature.

Table 1. Summary of Decomposition Measurements

fluid	$k \pm 1\sigma$ (s^{-1})	$t_{1/2}$ (years)	$t_{0.5-1.0\%}$[a] (days)	N[b]
n-pentane	$(4.7 \pm 0.7) \times 10^{-9}$	4.7	12.4	13
2-methylbutane	$(7.9 \pm 1.6) \times 10^{-9}$	2.8	7.5	8
2,2-dimethylpropane	$(1.5 \pm 0.3) \times 10^{-8}$	1.5	3.9	5
toluene	$(6.6 \pm 1.8) \times 10^{-9}$	3.3	8.9	7
benzene	$(6.3 \pm 20.3) \times 10^{-11}$	350	926	9

[a] $t_{0.5-1.0\%}$ = impurity increase rate. [b] N = Number of experimental measurements used to calculate rate constant.

After each run, the cells were solvent-rinsed with hexanes, toluene, acetone, and finally methanol using an ultrafine needle. Solvent rinsing was performed until each solvent was colorless as it exited the cell. Clean cells were heated to above 100 °C for at least 5 min to remove residual solvent.

Analytical Method. The samples were analyzed with a commercial gas chromatograph with split/splitless injection and flame ionization detection (30 m capillary column coated with a 1 μm film of 5% phenyl polydimethyl siloxane). Nitrogen was used as the carrier and makeup gas for all analyses.

Samples of the thermally stressed liquid n-pentane, 2-methylbutane, toluene, and benzene were withdrawn from the vessels by syringe and stored in chilled well vials (7 °C) until the analysis was performed. Aliquots (1 μL) of the fluids were injected onto the GC column using cooled syringes. The n-pentane and 2-methylbutane samples were separated isothermally at 50 °C. The benzene and toluene samples required temperature programming consisting of an 8 °C/min gradient from 55 to 250 °C. This final temperature was held constant for 30 min.

The gaseous 2,2-dimethylpropane samples could not be effectively withdrawn by syringe and were transferred directly from the reaction cells to the GC inlet. To facilitate the transfer, the reaction cells were heated to 165 °C to generate supercritical fluid 2,2-dimethylpropane (the critical temperature of this fluid is 160.6 °C). Once at the desired temperature, the cell was opened and an aliquot of the fluid was expanded into a six-port gas chromatographic sampling valve connected to the septum purge line of a split-splitless gas chromatographic injector.[35] All of the lines from the reaction cell to the sampling valve were heat-traced to prevent phase separation. The sample residing in the six-port valve at atmospheric pressure was then injected into the split-splitless inlet that was maintained at 275 °C. The analysis was done with the column maintained isothermally at 55 °C.

Fluid decomposition was observed from the decrease in the chromatographic signal of the pure fluid, accompanied by the appearance of new peaks in the chromatogram. The rate of fluid decomposition was determined from the logarithmic decrease in the pure fluid peak using peak area percent as a function of time.

Results and Discussion

The rate of decomposition of n-pentane, 2-methylbutane, 2,2-dimethylpropane, toluene, and benzene was measured at 315 °C. The results are summarized in Table 1. Sample chromatograms are shown in Figure 3 for the decomposition of n-pentane after 9.7 days. The change in the purity of n-pentane as a function of time is plotted in Figure 4.

Although at first glance it might appear that the fluids decompose slowly, on the order of years, it is important to view these rates (and half-lives) in the context of the expected or desired lifetime of a heat recovery unit. Moreover, we note that all of the fluids produced thermal decomposition products after being heated for only a few days. For example, the column labeled $t_{0.5-1.0\%}$ in Table 1 shows the time required to increase the concentration of decomposition products in the sample from 0.5 to 1.0%. This value ranges from approximately 4 days for 2,2-dimethylpropane to a projected 926 days for benzene.

Of the three pentane fluids studied, n-pentane showed the greatest fluid stability, with 50% of n-pentane loss projected to occur after 4.7 years. We found it required 9.2 days to increase the concentration of decomposition products by a factor of 2 above the concentration of impurities that were present initially. The n-pentane samples were recovered from the reaction cells as clear fluids. In some of the samples, after a reaction time of at least 9400 min, a gaseous product was observed to emanate from the opening of the reaction cell as the liquid sample was withdrawn; however, it is not known whether this product was present to any extent during the analysis of the fluid. In general, the impurities formed during n-pentane decomposition preceded n-pentane on the chromatogram. This suggests that n-pentane decomposed by fragmenting into smaller aliphatic chains.

The decomposition characteristics of 2-methylbutane are similar to those of n-pentane, although the rate of decomposition for 2-methylbutane is approximately 60% faster. Like n-pentane, the 2-methylbutane samples were recovered from the reaction cells as clear fluids and a gaseous product was present in the samples recovered after 9400 min or more. The majority of decomposition products eluted from the gas chromatograph before 2-methylbutane, with the exception of a single broad peak that emerged as a decomposition product for reaction times of 3.5 days and longer. This compound was identified as 3,3-dimethylpentane by gas chromatography mass spectrometry.

Of all the fluids measured, 2,2-dimethylpropane showed the greatest rate of decomposition at 315 °C. Although a few of the decomposition products preceded 2,2-dimethylpropane on the chromatogram, the majority of the impurities found in the sample eluted after the pure fluid.

Comparing the three pentanes, fluid stability decreased in the order n-pentane > 2-methylbutane > 2,2-dimethylpropane. This decrease in fluid thermal stability is not unexpected and is consistent with a free radical decomposition mechanism, where alkyl radical stability increases with the number of alkyl groups attached to the radical carbon.[36] The greater stability of the 2,2-dimethylpropane tertiary alkyl radical would also make possible the formation of later-eluting decomposition products by radical recombination and disproportionation.

While not directly of interest as pure ORC working fluids, benzene and toluene were studied as well. Earlier measurements on these fluids are generally not applicable in terms of experimental conditions.[37–40] Of the aromatic compounds studied, toluene decomposed with a rate comparable to that of 2-methylbutane, with half of the fluid loss projected to occur after approximately 3 years. In all of the toluene experiments, the fluid
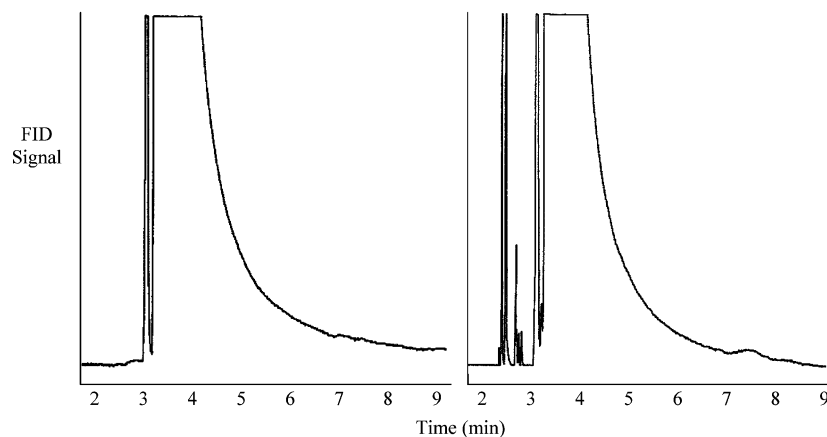
Figure 3. Gas chromatograms of *n*-pentane standard (left) and *n*-pentane sample after 9.7 days at 315 °C (right).
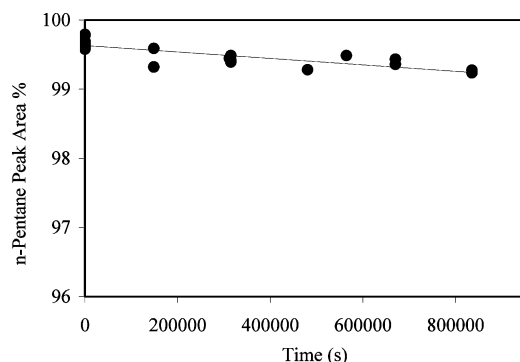

Figure 4. Decomposition of *n*-pentane at 315 °C.

recovered from the reaction cells had a distinctive yellow discoloration. Black particulates were observed in many of the samples, although the presence of particulates did not correlate with the length of the reaction. The primary impurities formed during toluene decomposition eluted much later than those for toluene and had retention times characteristic of biphenyl derivatives. Previously, the PVT properties of toluene were studied at temperatures from 75 to 450 °C at pressures to 35 MPa.[41] In that work, considerable decomposition of the toluene occurred at temperatures above 400 °C, with the majority of products identified as compounds containing two aromatic rings. As in the current study, the fluid was recovered from the high-temperature PVT experiments with a distinct yellow coloration.

Although benzene has some drawbacks with respect to health and safety, this fluid was found to have very high stability against thermal decomposition. This result was of course not unexpected. By comparison to the fluids containing an aliphatic group, the high overall resonance stabilization energy found in benzene safeguards the molecule from decomposition. In each of the nine benzene measurements, the fluid was recovered from the reaction cells as a clear liquid. Analysis of the samples revealed very few decomposition products present in the samples. In a previous study on the PVTsurface of benzene at pressures up to 35 MPa, a single decomposition product was observed whenever the temperature was maintained above 375 °C.[42] The decomposition product was identified as biphenyl and was present in amounts up to 0.08% (mass/mass) at the highest temperature, 450 °C. In the present study, biphenyl was identified as a decomposition product with a concentration from 0.001 to 0.004% (mass/mass), increasing with increasing reaction time.

In Table 1, it can be seen that the uncertainty associated with the decomposition rate of benzene is more than 3 times larger than the measured rate constant. With a projected decomposition half-life of 350 years, there is a great deal of uncertainty in the determination of the decomposition rate constant after a time period of only 2 weeks. Although a small biphenyl impurity was found in every sample of benzene recovered from the reaction cells, the uncertainty inherent in the rate constant predicts a decomposition rate that is essentially indistinguishable from zero. This statistical feature of the measured results is simply another indication of the relative stability of this fluid.

While the ORC we considered operates at 315 °C and 4.1 MPa at the hot reservoir, we desired an assessment of the effect of pressure on the decomposition rate. This desire recognizes the fact that, in a real cycle, pressure fluctuations can be quite pronounced, especially if the heat engine should encounter an upset condition. For this reason, we varied the cell-filling protocol to provide a variety of pressures in addition to the hot reservoir pressure. Cell pressure was calculated from the mass of fluid remaining in the cell at the termination of the experiment with the computer program previously described. Typical experimental pressures varied from 3.2 to 85 MPa. While this pressure range extends well beyond typical ORC working pressures, the extended range allowed general observations to be made on the effect of pressure on thermal decomposition for this application. We did not desire to study thermal decomposition at pressures much below the Rankine cycle pressure, nor was it practical to do so since the smaller sample quantities would have limited the quantity of fluid available for the analysis.

We found the decomposition to show little if any dependence on pressure. For example, in one experiment, three cells containing *n*-pentane were recovered from the thermal block after 1.7 days. Calculated cell pressures were found to be 7.9, 25.9, and 85.1 MPa. The level of impurities found in the samples at 7.9 and 85.1 MPa varied by only 0.1%. The sample recovered from the cell at 25.9 MPa contained 0.27% more impurities than the other two samples. In a more extreme example, three toluene samples recovered after 6.9 days had calculated cell pressures of 13.6, 35.8, and 250 MPa, yet the toluene recovered from the three cells had an average purity of 99.687 ± 0.027%. The variation in pressure for these toluene samples is the widest in this study, and the calculated pressure of 250 MPa is well outside the limits of the equation of state calculation;

however, these results exemplify the lack of correlation between pressure and fluid decomposition. All of the fluids studied showed a similar pressure independence. Furthermore, ideal gas Gibbs free energy minimization calculations[43] performed on these fluids also indicated that the products formed from the decomposition of each fluid are affected very little by the pressure of the system.

Conclusions

In this study, we have demonstrated the applicability of a simple ampule testing approach to assess the chemical stability of ORC working fluids. At 315 °C, fluid thermal stability for three pentane isomers was found to decrease in the order n-pentane > 2-methylbutane > 2,2-dimethylpropane. This decrease in fluid thermal stability corresponds with the expected order of increasing alkyl radical stability and is consistent with a free radical decomposition mechanism. Toluene was observed to have a decomposition rate similar to that of 2-methylbutane. Benzene was found to be the most thermally stable fluid measured due to the high resonance stabilization energy of its aromatic structure. While the time required for loss of 50% of the pure fluid was projected to be on the order of years for all fluids, small concentrations of decomposition reaction products were found in all of the heated fluids after as few as 2 days.

Acknowledgment

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