



Short communication

Pressure-controlled advanced distillation curve analysis and rotational viscometry of swine manure pyrolysis oil [☆]

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ABSTRACT

Pyrolysis is an effective method of converting agricultural byproducts to a tarry complex fluid suitable for use as a liquid fuel. While superficially similar in appearance to crude petroleum, pyrolysis oil contains significantly more oxygenated and nitrogenous compounds and up to 30% water by mass. These differences in composition affect both the heating value and viscosity of the fuel. We used the reduced-pressure advanced distillation curve (ADC) method to characterize the boiling point and composition of pyrolysis oil derived from swine manure. The swine manure pyrolysis oil was found to contain ~15% water by mass. Thermal cracking of the sample was observed near 300 °C at 3.5 kPa. The pyrolysis oil viscosity decreases exponentially as a function of temperature from 50 to 75 °C.

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1. Introduction

Over the past century, widespread adoption of petroleum-based fuels has transformed industrial economies around the world. Conventional petroleum is readily extracted, transported, and refined into a wide range of fuels. Recent concerns over the rising cost of conventional petroleum extraction due to diminishing reserves and the environmental effects of fossil fuel combustion have spurred a search for renewable sources of liquid fuels suitable for heating and transportation. Pyrolysis, or the breakdown of organic compounds at high temperatures in the absence of oxygen, is a promising approach to producing liquid fuels from a wide range of biomass sources [1]. Compared with first-generation biofuels, pyrolysis oils have higher energy density and do not compete with food crop production. Increased use of renewable liquid fuels is an energy policy objective of both the United States and the European Union [2,3].

The introduction of ASTM D7544, a standard specification for pyrolysis liquid biofuel used in industrial burners, marks an important milestone in the acceptance of pyrolysis oil as a renewable fuel [4]. The specification defines the heat of combustion, composition, kinematic viscosity, density, flash point, and pour point of grade D and G pyrolysis oils suitable for use in industrial burners.

While pyrolysis oil appears promising for meeting future energy needs, present methods of production yield a product that cannot be blended with petroleum-based transportation fuels. Means of separating, characterizing and upgrading pyrolysis oil are actively being sought today [5,6].

Archeological evidence shows that destructive distillation of wood, a form of slow pyrolysis, was used to obtain wood tar, a pyrolysis oil product, as early as the Paleolithic era [7]. The development of fast pyrolysis reactors in recent times has improved the yield of pyrolysis oil relative to pyrolysis gas and solid char formed from biomass [8]. Pyrolysis oil can be produced from a wide range of feedstocks, including waste products from timber production or agriculture [9–11]. Agricultural waste offers a ready supply of renewable biomass for pyrolysis oil production. Using agricultural waste to produce pyrolysis oil also reduces the environmental impact of contemporary intensive farming practices.

Intensive farming often generates concentrated waste products that can overwhelm local ecosystems if they are left untreated prior to disposal. One such example is swine manure slurries from large-scale feedlot operations [12]. The conversion of swine manure slurry to pyrolysis oil can simultaneously reduce the amount of waste that must be treated and produce a material that can be upgraded to fuels and chemicals. Characterizing the changes in the chemical and physical properties of swine manure pyrolysis oil as a function of temperature provides useful data in understanding how pyrolysis oils may be further refined or upgraded to meet future renewable fuel requirements.

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Pyrolysis oils, like other complex fluids, are challenging to characterize due to the large number of components that are present. Characterization processes in the laboratory, such as distillation, often have analogous processes in industrial-scale refining. The vapor–liquid equilibrium (VLE) of a complex fluid may be approximated by its volatility during distillation. Distillation of a complex fluid can yield experimental data useful in characterizing its physical and chemical properties.

The advanced distillation curve (ADC) method offers significant advantages over earlier approaches to complex fluid characterization, featuring (1) a composition-explicit data channel for each distillate fraction (for both qualitative and quantitative analyses), (2) temperature, volume and pressure measurements of low uncertainty that are true thermodynamic state points suitable for equation of state development, (3) an assessment of the density and enthalpy as a function of distillate volume fraction, (4) trace chemical analysis of each distillate fraction, and (5) a corrosivity assessment of each distillate fraction [13–15]. ADC data are consistent with a century of literature on the thermophysical properties of complex fluids. The method has been used to characterize *n*-alkanes [16], simple azeotropes [17], gas turbine fuels [18–23], diesel and biodiesel fuels [24–30], gasolines [31–33], rocket propellants [18,34–36], crude oils [37–39], and pyrolysis oils [40]. Unlike the conventional distillation curve, fuel volatility or vapor–liquid equilibrium data, ADC data can be modeled with an equation of state [41–46]. This short communication summarizes the application of the reduced-pressure ADC method to swine manure pyrolysis oil previously characterized at atmospheric pressure [40], and provides additional data in the study of pyrolysis oils.

2. Materials and methods

2.1. Materials

Pyrolysis oil derived from swine manure slurry was provided by Professor Yuanhui Zhang at the University of Illinois at Urbana-Champaign [47–49]. The pyrolysis oil was produced by reacting swine manure slurry with an initial charge of 0.34–2.76 MPa of carbon monoxide at an operating temperature of 275–350 °C in a 1.8 L T316 stainless steel reactor. Additional details of the swine manure slurry preparation and thermochemical conversion process have been published previously [47,50]. The resultant pyrolysis oil has a tar-like appearance and has a strong smoky odor. The sample was stored at ambient temperature and analyzed as received.

The pyrolysis oil is mostly insoluble in *n*-hexane and toluene, but dissolves completely in acetone. The acetone solvent used in this study was purchased from a commercial supplier and determined to be approximately 99% (mass/mass) pure through gas chromatography with mass spectrometric detection (GC–MS).

2.2. Advanced distillation curve method

The reduced-pressure ADC apparatus and sampling method have been described in detail in several earlier works [16,18,20,31,51]; a short description of particular steps used in this study is noted here for clarity. Due to the viscous and opaque nature of the sample, the initial volume of the pyrolysis oil in the boiling flask (kettle) was calculated from its mass and its density at ambient temperature (0.787 g/cm³, with a combined expanded uncertainty of 0.036 g/cm³, as measured through pycnometry). The mass of the boiling flask was measured on an analytical balance prior to and after sample introduction; the sample mass was calculated by difference. Estimated uncertainties were added in quadrature to yield the combined expanded uncertainties that are reported in the results and discussion.

Two thermocouples were used to monitor the vapor temperature at the bottom of the distillate take-off position (T_h) in the distillation head and the liquid temperature (T_k) in the kettle concurrently. An aluminum heating enclosure was used to increase the fluid temperature uniformly and at a constant rate using prior distillation data as a guide. The distillate vapor travels from the kettle through the distillation head and enters an air-cooled condenser, where it condenses into a liquid condensate. The liquid condensate then flows through a sampling adapter before entering a volume-calibrated graduated receiver. The distillation curve of the sample is determined by measuring changes in the kettle temperature as a function of distillate volume.

A commercial vacuum controller was connected to the apparatus to measure and control the system pressure. The controller uses a piezoresistive transducer and continuously regulated proportional valves to evacuate and vent the system for pressure control. The pressure controller can maintain a set pressure between 1 and 83 kPa (0.1 kPa resolution, 0.1 kPa estimated uncertainty). Pressure readings were calibrated by measuring the vapor pressure of deionized water as a function of temperature. A liquid nitrogen cold trap was placed between the apparatus and the pressure controller to condense any vapors that might escape the apparatus.

A gas reservoir containing 1 L of carbon dioxide was connected directly to the vacuum controller as a safety measure. The volume of the carbon dioxide gas in the reservoir exceeds the total system volume of the ADC apparatus. If the system must be brought to atmospheric pressure quickly, the carbon dioxide from the reservoir prevents air from coming into contact with the hot pyrolysis oil sample in the boiling flask.

2.3. Gas chromatography with mass spectrometric detection (GC–MS)

Small aliquots (10 μL) of the distillate were withdrawn at predetermined distillate volume fractions with a pressure-balanced chromatography syringe in the receiver adapter hammock and dissolved in a fixed quantity of acetone inside an autosampler vial. The diluted aliquots were analyzed using GC–MS (30 m column with an 250 μm inner diameter coated with a 0.25 μm film of 5% phenyl-95% dimethylpolysiloxane, helium carrier gas at 48.3 kPa or 7 psi inlet pressure, split ratio of 50:1, temperature program starting with an isothermal soak at 75 °C for 1 min, followed by a slow ramp to 275 °C at a heating rate of 5 °C/min and a fast ramp to 305 °C at a heating rate of 15 °C/min) [52]. The fluid components were characterized through mass spectrometric detection and identified using the NIST 11 Mass Spectral Library [53].

2.4. Rotational viscometry

A commercial rotating cylinder viscometer (inner spindle diameter 1.175 cm, outer cylinder diameter 1.900 cm) was used to measure the kinematic viscosity of the bulk fluid at 6 and 12 rpm. The viscometer was calibrated using a certified poly- α olefin reference fluid. The bulk pyrolysis oil was first added to an aluminum sample cylinder, which was then loaded into a commercial heating enclosure. The pyrolysis oil was heated to 70.0 °C prior to spindle insertion. Its viscosity was measured as a function of temperature based on multiple steady-state values at 5 °C intervals, as the enclosure temperature was decreased from 70 to 50 °C.

3. Results and discussion

3.1. Boiling point and composition as a function of distillate volume

A typical ADC measurement begins with visual observation of the initial boiling conditions (onset of bubbling, sustained bubbling

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