Optimization of Distillation Curve Measurements to Accurately Characterize Gasoline Fuel Composition

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Introduction

The performance of a gasoline blend can be characterized by its ability to vaporize under various conditions. Properties used to quantify the vaporization or volatility of a fuel include the fuel’s distillation curve, Reid Vapor Pressure (RVP), and temperature for a vapor-to-liquid ratio of 20 (T90). These volatility properties are useful metrics for designing green gasoline fuels (composed of chemical components derived from renewable, biological materials) that mimic the performance of traditional gasoline blends.

Distillation curves are of particular interest because by closely matching a fuel’s distillation curve, all of a fuel’s volatility properties can be closely matched. The current work aims to optimize the experimental measurement of distillation curves to accurately characterize the vaporization process of a fuel and implement the distillation curves in a model used to design green gasoline fuels with volatility properties similar to those of traditional gasoline.

ASTM D86 Distillation Curve

ASTM D86 is the standard specification for the batch distillation of gasoline, diesel, and jet fuels used to specify fuel requirements. It outlines a procedure for creating “D86” distillation curves and specifies the configuration of a standard distillation apparatus.

The D86 procedure utilizes a 100 mL liquid fuel sample, which is boiled, condensed, and collected in a graduated cylinder. The temperature of the vaporized fuel and the collected volume are simultaneously recorded at regular intervals. The result is an ASTM D86 distillation curve:

By matching a fuel’s distillation curve, one can closely match other volatility properties (RVP and T90 values), as well as various operational parameters [2]:
- Vehicle driveability
- Fuel system freezing or vapor lock
- Flashpoint
- Emissions

Experimental Setup

A Koehler 45200 manual distillation apparatus was used to distill each fuel mixture in accordance with the ASTM D86 distillation standard. The setup was modified to incorporate two high-accuracy platinum resistance temperature detector (RTD) probes whose temperatures were recorded continuously on a data acquisition system. Volume measurements were recorded at 5 mL intervals in conjunction with the continuous temperature measurements.

Shortcomings of ASTM D86

Thermodynamic relations can be used to calculate equilibrium distillation curves by tracking the vapor-liquid equilibrium process as a fuel vaporizes. These equilibrium curves are a thermodynamically accurate description of the vaporization process of a fuel. Curves measured according to ASTM D86 do not match these theoretical equilibrium curves:

The disagreement between the equilibrium thermodynamics and ASTM D86 distillations is due to the following:
1. Location of the temperature probe
   D86 measures vapor temperature, not liquid fuel temperature. Vapor temperature is highly sensitive to temperature probe location and ambient conditions.

2. The volume measured in the graduated cylinder does not represent the total volume of evaporated fuel. This is due to fuel vapor present in the lines between the distillation flask and graduated cylinder receiver. This discrepancy is termed “Dynamic Holdup.”
3. Required use of a mercury thermometer
   Mercury thermometers have limited temporal resolution and add additional heat transfer losses.

Dynamic Holdup Model

To more accurately measure equilibrium distillations in the modified setup, the time-resolved liquid temperature data were used to develop a model to account for the dynamic holdup of the evaporated sample inherent in the D86 distillation process.

Steps necessary to calculate dynamic holdup:
1. Identify Initial Boiling Point (IBP)
   The IBP was taken to be the minimum of the second derivative of liquid temperature with respect to time, assessed over the first 5-10 minutes of the distillation.

   This technique was validated through comparison of the predicted IBP to the theoretical IBP and visual confirmation of the initial boiling point.

2. Approximate rate of distillation
   By acquiring time-resolved data, each volume point of the D86 distillation curve can be associated with a point in time. This allows for the approximation of distillation rate (mL/sec) between data points.

   Once the IBP is accurately identified, the instantaneous volume of evaporated fuel can be calculated by integrating the distillation rate over time. Subtracting each D86 volume from the calculated, instantaneous volume at that same instance in time yields the dynamic holdup.

Application of Equilibrium Curves: Fuel Design

Experimental equilibrium distillation curves can be used to design green gasoline fuels with volatility properties matched closely to those of petroleum-derived gasoline. Previous work from our group has shown that 4-component mixtures are the least complex mixtures capable of accurately matching gasoline volatility [3]. A volatility model was previously developed to optimize the combination of four chemical components (chosen from a library of 35 potential components) to yield an equilibrium distillation curve that matches a target fuel’s distillation curve.

When the experimental equililibrium curve (calculated using the dynamic holdup model) for EPA Tier II EEEE gasoline is fed into the volatility model, the model generates a four-component fuel mixture whose equilibrium curve matches that of EEEE gasoline.

Conclusions & Future Work

Conclusions:
- By applying a dynamic holdup shift to liquid temperature distillation curves, it is possible to experimentally measure equilibrium distillation curves
- When used in conjunction with a volatility property-matching optimization model, equilibrium curves can be used to design gasoline-like fuels with desirable volatility properties

Future Work:
- Develop a heat transfer model to derive equilibrium curves directly from D86 vapor distillation curves
- Use dynamic holdup model and volatility property-matching optimization model to aid in the design of green gasoline fuels