Physical Properties and Process Conditions Affecting Hydrocarbon Measurement

James E. Gallagher, P.E.
Savant Measurement Corporation

INTRODUCTION

Measurement is the basis of commerce between producers, royalty owners, transporters, process plants, marketers, state and federal governmental authorities, and the general public. In fact, accurate measurement of hydrocarbon fluids and materials has a significant impact on the Gross National Product of exporting and importing countries, the financial performance and asset base of global companies, and the perceived efficiency of operating facilities. The need for accurate fiscal measurement is obvious. Given the present or future levels of the cost of these critical resource materials, one can quickly quantify the material and economic value that is associated with each ± 0·01 per cent systematic uncertainty that might unknowingly exist in the measurement systems.

Measurement errors can have both near-term and long-term impact on corporate profits. Inaccurate measurement may result in loss of customers, adverse publicity, potential penalties, and legal liabilities. In short, equitable and accurate measurement is essential to business. It affects the validity of financial and operating reports as well as the corporate reputation.

For reasons such as these, it is essential that material quantity and quality measurements are precise and accurate with minimal bias errors. Furthermore, it is incumbent upon those involved in custody transfer to establish and maintain the traceability chains that link their measurements to appropriate domestic and international standards. In this manner, fiscal transfer of materials can be done equitably with the confidence of both seller and buyer alike.

The capital and operating resources applied to fiscal transfers must be commensurate with the total cost of measurement – the capital cost of technology, the operating cost of technology, industry practice or standards, regulatory compliance and the total fiscal exposure or risk (commodity value times throughput).

An understanding of the process (operating and fluid) conditions as well as the physical properties of the fluid are fundamentally important to properly design these measurement facilities.

I. APPLICABLE FLUIDS

Fiscal measurement applies to steady-state mass flow conditions for fluids that, for all practical purposes, are considered to be clean, single phase, homogeneous and Newtonian under the operating conditions of the facility.

All gases, most liquids and most dense phase fluids associated with the petroleum, petrochemical and natural gas industries are usually considered to be Newtonian fluids.

II. PHASE BEHAVIOR

Fluids are classified into four phase regions –

- ⇨ Liquid
- ⇨ Gas or vapor

- ⇨ Dense phase or supercritical , and
- ⇨ Two-phase

A salient point is that fiscal measurement is applicable for single-phase fluids (liquid, gas or dense phase).

The **liquid phase** region has a definite volume but no definite shape. It will assume the shape of the container in which it is placed but will not necessarily fill that container. The liquid phase region exhibits low fluid compressibility and high mass density values.

A **gas or vapor phase** region has no definite volume or shape and will completely fill the container in which it is placed. The gas phase region exhibits high fluid compressibility and low mass density values.

Assuming a constant composition, the mass density of a gas is lower than the mass density of a liquid.

A **dense or supercritical phase** region has no definite volume or shape and will completely fill the container in which it is placed. The dense phase region exhibits high fluid compressibility and high mass density values. These values vary as a function of the fluid's pressure and temperature values. The dense phase region is defined as the region whose pressure exceeds the critical value (Pc).

The **two-phase region** has no definite volume or shape and will completely fill the container in which it is placed. The two-phase region contains fluid in both gas and liquid states simultaneously. If the fluid is left in the two-phase region, it will eventually move to the gas dewpoint curve due to conservation of energy.

- ⇨ For pure components, the two-phase region is well known and varies as a function of pressure and temperature.

- ⇨ For multiple component fluids, such as natural gas, the two-phase diagram is less well known and varies as a function of pressure, temperature and composition.

There are several important terms associated with the two-phase envelope –

Critical Point is the pressure (Pc) and temperature (Tc) at which the properties of the liquid and gas phases become identical ('C').

Cricondenbar is the maximum pressure at which liquid may exist ('N'). For singe component compositions, or pure fluids, the cricondenbar and the critical point are identical.

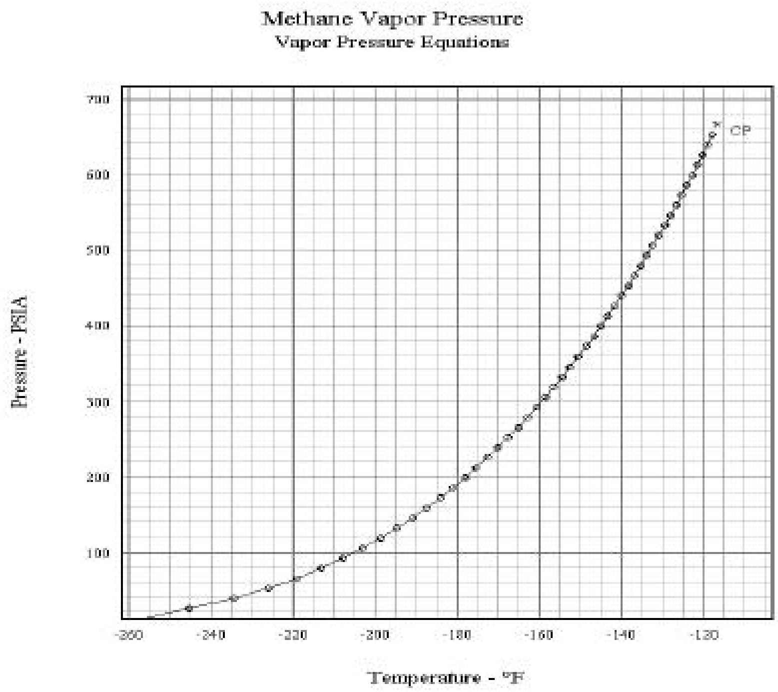
Cricondentherm is the maximum temperature at which gas and liquid may co-exist in equilibrium ('M').

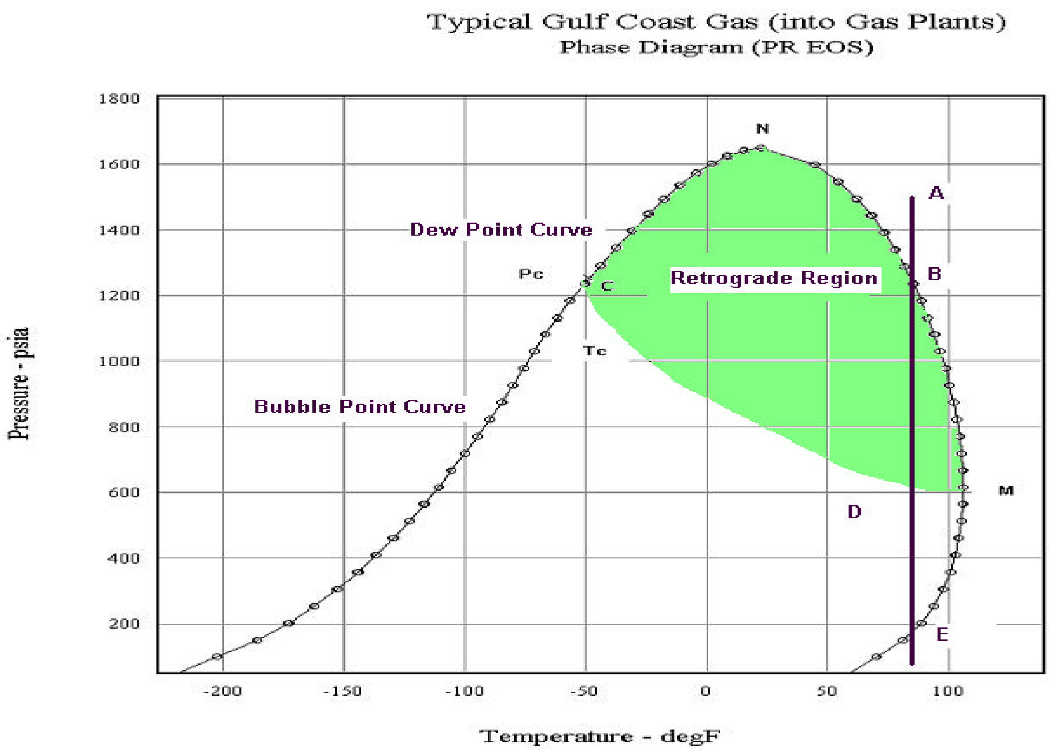
Retrograde region is the area inside the phase envelope where condensation of liquid occurs by lowering pressure or increasing temperature. For singe component compositions, or pure fluids, a retrograde region does not exist.

Quality lines are those lines showing constant gas volume weight percentages that intersect at the critical point ('C') and are essentially parallel to the bubble point and dew point curves.

Bubble point curve is the curve separating the liquid region from the two-phase region.

Dew point curve is the curve separating the gas region from the two-phase region.





Line ABDE represents a typical isothermal (constant temperature) retrograde condensation process. Point A represents the single dense phase fluid outside the phase envelope. As pressure is lowered, point B is reached where condensation begins. As pressure is lowered further, additional liquid forms due to the change in the slope of the quality lines. The retrograde area is governed by the inflection points of the quality lines. As the process continues outside the retrograde area, less and less liquid forms until the dew point is reached (point E). Below point E no liquid is present in the fluid stream.

Natural gas gathering system condensate is comprised of produced condensate, retrograde condensate and retrograde vaporization.

Production condensate is measured and injected as liquid condensate into the natural gas gathering pipeline. Due to the USA's EPA limits on RVP of crude oils, liquid condensate production is typically injected into the natural gas pipeline gathering system. The gas plant, located at the terminus of the system, is designed to separate produced condensate, retrograde condensate, retrograde vaporization, free water, particulates, pipeline rouge and merchantable dry clean natural gas from the natural gas gathering system.

The phenomenon of liquid formation by isothermal expansion of a single-phase fluid is ***retrograde condensation***. Stated another way, for dense-phase mixtures the liquid forms as a result of pressure reduction of the fluid.

The term *retrograde condensation* may be applied to isobaric conditions due to temperature variations.

The phenomenon of liquid formation by isothermal compression of a single-phase fluid is ***retrograde vaporization***. Stated another way, for gas-phase mixtures the liquid forms as a result of pressure increase of the fluid.

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III. FLUID PHYSICAL PROPERTIES

Fluid physical properties are of fundamental importance and must be ascertained before any serious measurement design or analysis.

The physical properties ***crude oils*** are -

- Fluid Density (ρ_b, ρ_{tp})
- Absolute Viscosity (cP), or Kinematic Viscosity (cSt)

- API Gravity (API@60)
- Pour Point (°F or °C)
- Cloud Point (°F or °C)
- Wax Content (wt %)
- Reid Vapor Pressure (psia)
- Phase envelope or bubble point prediction

- Sulfur Content (wt %)
- H2S Content (ppm wt)
- Sediment and Water Content (vol. %)
- TANE or acid and neutralization levels (mg KOH/gm)
- Salt Content (lbm/M Bbl)
- Metals in whole Crude and Pitch (ppm wt)
- Contaminants (organic chloride, methanol, and so forth)

The physical properties for ***refined products*** (gasoline, diesel, jet fuel, lube oils) are -

- Fluid Density (ρ_b, ρ_{tp})
- Absolute Viscosity (cP), or Kinematic Viscosity (cSt)

- API Gravity (API@60)
- Pour Point (°F or °C)
- Reid Vapor Pressure (psia)

- Phase envelope or bubble point prediction

- Water Content (units of measure specific to fluid application)
- Sulfur Content (units of measure specific to fluid application)
- Contaminants (bacteria and so forth)

The physical properties for ***natural gas*** are -

- Gas composition (mole percent of $C_1 – C_9$, CO_2, N_2)
- Fluid Density (ρ_b, ρ_{tp})
- Absolute Viscosity (cP), or Kinematic Viscosity (cSt)
- Isentropic Exponent (for orifice meters)
- Speed of Sound (for MUSMs)

- Energy content (BTU per MCF)
- Relative Density @ 60°F

- Phase envelope or dewpoint curve for normal composition
- Hydrate formation (upstream of gas plants)
- Water content (lbm/MCF)
- Sulfur content (grains per 100 SCF)
- H2S content (grains per 100 SCF)

The physical properties for ***condensate and LPG*** are -

- Composition (mole percent of $C_1 – C_9$, CO_2, N_2)
- Fluid Density (ρ_b, ρ_{tp})
- Absolute Viscosity (cP), or Kinematic Viscosity (cSt)
- Isentropic Exponent (for orifice meters)

- Phase envelope or bubble point prediction
- Water Content (units of measure specific to fluid application)
- Sulfur Content (units of measure specific to fluid application)
- H2S Content (units of measure specific to fluid application)

IV. PROCESS (OR OPERATING) CONDITIONS

The operating or process conditions for the metering application are also critical design parameters. In certain situations, the metering facility may be relocated due to the process conditions and the dynamics of the physical properties. In other situations, the meter facility may require special elastomeric materials, operating procedures, or meter calibration frequencies to control the impact of the process conditions on the uncertainty of the measurements.

Design Parameters

To design and operate an accurate flowmetering application, an ***envelop*** of the following parameters should be assembled and validated after startup for ***liquid and dense phase measurement facilities*** -

- Mass Flowrate (lbm/hr) - maximum, minimum, normal
- Volumetric Flowrate at Reference Conditions (BPH) - maximum, minimum, normal

- Pressure (psig) - maximum, minimum, normal
- Temperature (°F) - maximum, minimum, normal
- Fluid Density (ρ_b, ρ_{tp}) - maximum, minimum, normal
- Viscosity (cP or cSt) - maximum, minimum, normal

- Isentropic Exponent (applicable for compressible orifice measurement)

- Meter Piping and Header Velocity (fps) - maximum, minimum, normal
- Prover Velocity (fps) - maximum, minimum, normal
- Sampling System Velocity (fps) - maximum, minimum, normal

To design and operate an accurate flowmetering application, an ***envelop*** of the following process conditions should be assembled and validated after startup for ***gas and dense phase measurement facilities*** -

- Mass Flowrate (lbm/hr) - maximum, minimum, normal
- Volumetric Flowrate at Reference Conditions (MCFH) - maximum, minimum, normal

- Pressure (psig) - maximum, minimum, normal
- Temperature (°F) - maximum, minimum, normal
- Fluid Density (ρ_b, ρ_{tp}) - maximum, minimum, normal
- Viscosity (cP or cSt) - maximum, minimum, normal
- Isentropic Exponent (applicable for compressible orifice measurement)
- Speed of Sound (for MUSMs)

- Meter Piping and Header Velocity (fps) - maximum, minimum, normal
- Prover Velocity (fps) - maximum, minimum, normal (if applicable)
- Sampling System Velocity (fps) - maximum, minimum, normal

Other Process Parameters

Other process or operating parameters and preventive maintenance programs to consider in the design and operation are -

- Pseudo Fully Developed Flow (for inferential flowmeters)
- Cleanliness of Stream (particulates) - impact on measurement system
- Pigging Frequency - impact on measurement system
- Multiphase (retrograde condensate, etc.), slug catchers, coalescing filters, impact on measurement system
- Wax Formation – amount and disposal of wax, impact on measurement and transportation system
- Hydrate Formation - impact on measurement and transportation system
- Hydrochloric Acid Formation
- Sulfuric Acid Formation
- CO_2 stress corrosion phenomena
- Elastomer Compatibility (for valves and other equipment)
- Prover coating compatibility
- Presence of Drag Reducing Agent – impact on measurement and transportation system
- Inhibitor Program
  a) Anti-floculation agents
  b) Oxygen scavengers
  c) Fungicides or Biocides (to control bacteria)
  d) Internal corrosion inhibitors

V. TYPICAL FLUIDS

To fully understand the significance of fluid and process conditions on the measurement system, fluids can be grouped into three categories –

- **Raw Materials** - crude oil, condensate, natural gas upstream of gas plants, etc.

- **Intermediate Products** - EP mixes, raw make, chemical feedstocks, etc
- **Refined Products** - gasoline, turbine fuel, diesel fuel, fuel oil, natural gas downstream of gas plants, etc

Raw Materials

Raw materials are fluids that are produced from natural reservoirs, processed for transportation reasons and transported to a plant or facility that converts the raw material into intermediate and/or refined products. The salient point is that raw materials are converted to intermediate or refined products by a plant, refinery or process facility.

Crude oil and natural gas (upstream of gas plants) are raw materials whose ‘loose specifications’ are based on the transportation and end user requirements.

Other raw materials are production condensate, drip gasoline, and NGLs upstream of processing facilities. These products are transported to the process facilities (gas plant, refinery or chemical plant) based on ‘loose’ raw material specifications.

Intermediate Products

Intermediate products are materials not completely processed for commercial applications. These products are sold to other process plants, refineries or chemical plants based on ‘loose’ specifications to satisfy transportation and end user specifications. Again, the salient point is that intermediate products are converted to refined products by a plant, refinery or process facility.

Refined Products

Refined products are materials that have been processed to satisfy well-defined product specifications established by the transportation, end user, or federal regulations.

For refined products, industry specifications, governmental specifications and regulations exist for the following refined products - military jet fuels, gasoline RVP seasons for EPA compliance, sulfur levels in diesel fuels for ‘on-road’ versus ‘off-road’ commercial applications.

Material quality specifications and the exposure varies with the fluid or material involved in the fiscal transaction. Since measurement personnel are involved in the quantity determination, normally these same people are assigned duties to ensure compliance with the minimum specifications for the transferred material and compliance with the applicable governmental regulations.

Environmental Regulations – Atmospheric Storage of Liquids

State enforced EPA regulations regarding atmospheric storage tanks should be addressed. While the regulations exclude crude oil production tanks, the pipeline, storage facility and refinery atmospheric storage tanks are required to meet the EPA mandates. Normally, the measurement personnel are assigned the responsibility to ensure compliance to the emissions’ regulations through the measurement manual and connection requirements, which are policy.

Materials with an RVP of 8.6 psia or less are accepted at all times. Materials that do not exceed an RVP of 9.6 psia are accepted during the winter months (October 1 through April 30). Materials exceeding the RVP of 9.6 psia cannot be transferred from the production facility. Of course, exceptions may be made for special conditions as long as the material contained in the atmospheric pipeline or refinery storage tank does not violate the EPA requirements. Again, management through delegation of authorities and policy statements should be involved in each incident.

Crude Oil – A Raw Material

Crude oils are raw materials generally classified based on the sulfur, metals, TANE and salt content.

The classifications below are based on refinery design and their impact on refinery operations.

	Sulfur (wt, %)	Metals (V+N in pitch, ppm)	TANE (mg KOH/gm)	Salt (lbm/MBbl)
1) Sweet – Lo Metals	< 0.50	≤ 100	≤ 1.0	≤ 75
2) Sweet – Hi Metals	< 0.50	≤ 250	≤ 1.0	≤ 75
3) Intermediate	≥ 0.50 ≤ 1.00	≤ 550	≤ 1.0	≤ 75
4) Sour	> 1.00 ≤ 2.00	≤ 1,200	≤ 1.5	≤ 75
5) Hi Sour	> 2.00	≤ 1,200	≤ 1.5	≤ 75

'Sweet' refineries cannot efficiently or safely consume 'sour' crude oil. Although some 'sweet' refiners blend 'sour' crude oil with 'sweet', they assume the accountability on their operations.

The content of two metals, the vanadium and nickel content, can adversely affect the efficiency and safety of the refinery process.

The TANE content, or acid level, can adversely affect the efficiency and safety of the refinery.

The salt content can adversely affect the efficiency of the refinery process (the desalter upstream of the distillation process and downstream of the refinery tankage).

Crude oil's pricing structure, merchantability and transportation impacts are determined by the following crude oil quality parameters:

- API Gravity
- RVP
- Sulfur Content
- Pour Point
- Viscosity
- H_2S Content
- Metals Content
- Neutralization Number
- Salt Content
- Carbon Residue
- Wax Content
- Distillation Curve

A crude oil parameter not used to classify its merchantability, but is significant to operating personnel safety, is the H_2S content. It is important to note that H_2S is present only for "intermediate", "sour" or "hi sour" crude oil classifications.

The quality of crude oil impacts the merchantability to the refiner. In other words, the refiner's economics are based on the crude oil assay. In some cases, the refiner will pay a premium for specialty crude oils since they improve the efficiency or economics of the refinery process units.

Crude oil is grouped into two major categories for transportation - fungible (or commingled) streams, and batched (or segregated) streams.

Fungible streams consist of various crude oils gathered together in the production areas. As a result, the fungible stream is defined as that represented at the termination point of the gathering system. The termination point is defined as where it enters a major transportation and storage system or a gathering system that terminates at a refinery. The pricing structure and crude oil merchantability are based on the crude oil assay representative at the termination point.

Fungible streams may also be various crude oils that have similar crude oil assay results that are commingled along the transportation system. These streams usually involve large throughputs such as Light Louisiana Sweet (LLS) that is gathered from fields in the Gulf of Mexico, or West Texas Sour (WTS) that is gathered from the onshore fields in Texas and New Mexico.

Batched or segregated streams are incompatible fungible streams or dedicated production streams. For example, WTS is incompatible with LLS; likewise Algerian condensate is incompatible with Mexico's Mayan crude oil.

Two facets of crude oil quality --- degradation and contamination, economically impact the refiner.

Degradation is a process that occurs when oil is transported through a transportation system. Crude oil degradation occurs due to interfacial mixing, tank bottoms, dock lines, tank lines, headers and so forth. This event can occur as a result of normal operations and abnormal operations. Batched streams are segregated along the transportation system and stored in dedicated storage tanks to minimize degradation of the stream. In addition, appropriate batch cutting operations are required to minimize degradation of the crude oil quality.

Crude oil contamination is the contamination of crude oil by an outside ingredient prior to, or after entry into the transportation system. Crude oil contamination occurs as a result of intentional or accidental dumping of lube oils, greases, lead compounds, PCBs, cleaning solvents, and chemical by-products. Contaminants can affect the efficiency and safety of the transportation system, the refinery and the environment.

Crude oil trucks and barges formerly in chemical or waste service, not properly cleaned, have caused accidental contamination. Inappropriate chemicals associated with the production of crude oil have caused accidental contamination.

Natural Gas – Raw Material and **Refined Product**

The distinction of whether natural gas is a raw material or refined product is based on whether the natural gas has been completely processed by a gas plant.

The gas compositions between the inlet and outlet of the gas plant are significant in light of the physical properties and the two-phase phenomena. Gas plant economics are based on the price of the other raw materials (condensate and so forth), intermediate products, refined products and natural gas. As such, the composition exiting the plant will vary due to the commodity value of the various components and the gas plant design.

Typical gas compositions at the inlet and outlet of a gas plant are shown in the following tables. To impress on the reader the impact of this processing, the phase envelopes for the inlet and outlet of the gas plant have been prepared for these compositions.

Natural Gas – A Raw Material

The gas gathering system terminates at the inlet of the gas plant. As a result, the fluid contains several components – free water, production condensate, retrograde condensate, particulates, pipeline rouge and natural gas.

The gas plant removes water, H_2S, sulfur, particulates and pipeline rouge from the raw material.

Intermediate and Refined Products from Natural Gas

Condensate and retrograde condensate are removed by the processing facility and converted into ‘other raw materials, ‘intermediate products’, or ‘refined LPG products’ (spec propane and spec butane).

Natural Gas – A Refined Product

Since natural gas is a refined product at the exit of the gas plant, the processing facility removes any component that negatively affects the quality of the fungible stream. A quality specification must be met to ensure the natural gas exiting the plant confirms to the fungible steam’s requirements (BTU, H_2S, sulfur and so forth)

The gas transmission system begins at the exit of the gas plant. By definition ‘transmission quality’ natural gas is a refined product. The transportation system and end users establish these specifications.

			DSG Composition - Mole Percent	
			Inlet of Gas Plant	**Exit of Gas Plant**
Paraffinic Hydrocarbons				
1	CH4	Methane	88.023	96.5222
2	C2H6	Ethane	5.824	1.8186
3	C3H8	Propane	3.292	0.4596
4	C4H10	iso-Butane	0.936	0.0977
5	C4H10	n-Butane	0.537	0.1007
6	C5H12	iso-Pentane	0.249	0.0473
7	C5H12	n-Pentane	0.236	0.0324
8	C6H14	n-Hexane	0.149	0.0664
9	C7H16	n-Heptane	0.189	-
10	C8H18	n-Octane	0.098	-
11	C9H20	n-Nonane	0.036	-
12	C10H22	n-Decane	-	-
Non-Hydrocarbons				
22	N2	Nitrogen	0.2620	0.2595
23	CO2	Carbon Dioxide	0.1690	0.5956

Sum	100.0000	100.0000	
Sum Ethane +	5.7220	0.8041	C3H8 - C10H22
Mw_{gas}	19.1542	16.7994	lbm / [lbm * mol]
G (dry gas)	0.6630	0.5810	Real Gas Density (G)
Zb_{gas}	0.997022	0.997840	@14.73 psia and 60 degF
RHOb	0.050742	0.044468	lbm/ft3 @ 14.73 psia and 60 degF
Gross Hv^{id}	1,171.1	1,034.0	Btu/ft3 @ 14.73 psia and fuel as ideal gas