

Refinery Intermediate Product

Literature Review

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Final Report

Prepared for

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List of acronyms and abbreviations

AGO	Atmospheric gas oil
API	American Petroleum Institute
bbbl	Barrel
BPCD	Barrels per calendar day
BPD	Barrels per day
BTX	Benzene, toluene, xylene
CBI	Confidential business information
CBO	Carbon black oil
CHGO	Coker heavy gas oil
CLGO	Coker light gas oil
CNF	Catalytic naphtha fractionator
cP	Centipoise
CPPI	Canadian Petroleum Products Institute
cSt	Centistoke
DAO	Deasphalting oil
DIAL	Differential absorption light detection and ranging
FBP	Final boiling point
FCCU	Fluid catalytic cracking unit
FIA	Fluorescent indicator adsorption
GC-MS	Gas chromatography-mass spectroscopy
HCCN	Heavy catalytic cracked naphtha
HAP	Hazardous air pollutant
HDS	Hydrodesulfurization
HOOPS	Hoover Offshore Oil Pipeline System
HOST	Heavy Oil Storage Tank Committee
HPG	Hydrogenated pyrolysis gasoline
HPLC	High-performance liquid chromatography
HSR	Heavy straight run
HVGO	Heavy vacuum gas oil
IBP	Initial boiling point
LCCO	Light cracker cycle oil
LCO	Light cycle oil
LGO	Light gas oil
LPG	Liquefied petroleum gas
LT	Less than
LVGO	Light vacuum gas oil
MSDS	Material safety data sheet
MW	Molecular weight
n/a	Not available
nD20	Refractive index at the sodium D line at 20°C
NMVOC	Non-methane volatile organic compound
OMB	Office of Maintenance and Budget
OPF	Olefins plant feed
Pa	Pascal
PAD	Petroleum Administration for Defense

PAH	Polyaromatic hydrocarbon
PNA	Polynuclear aromatic
psia	Pounds per square inch absolute
ROSE	Residuum oil supercritical extraction
RVP	Reid vapor pressure
SDA	Solvent deasphalting
SR	Straight run
STARS	State of Texas Air Reporting System
TBP	True boiling point
TCEQ	Texas Commission on Environmental Quality
TVP	True vapor pressure
UN ILO	United Nations International Labour Organization
US EIA	US Energy Information Administration
US EPA	US Environmental Protection Agency
US NTP	US National Toxicology Program
VBA	Visual BASIC for applications
VGO	Vacuum gas oil
VOC	Volatile organic compound

Final Report

Introduction

This report is the Task 4 deliverable: final report for the Texas Commission on Environmental Quality (TCEQ) project “Refinery Intermediate Product Literature Review” (TCEQ PGA No. 582-13-30089-FY14-15, TCEQ Tracking No. 2014-22-PCR# 42253). The first deliverable was the Grant Activity Description with the quality assurance project plan, the second deliverable was a literature search review, and the third deliverable was a draft report.

Methods for calculating estimates of petroleum-related storage emissions focus on crude oil and refinery products; emissions from storage tanks holding intermediate products at refineries are not generally included in illustrations of tank emissions. For example, the US Environmental Protection Agency’s (US EPA’s) TANKS 4.0 software does not have refinery intermediate product streams in its speciation library.

This omission may be partly because of the variation in intermediate products. The composition of these products varies depending on the crude charge, refinery configuration and processes, and on operating conditions that are adjusted as markets change. Therefore, there is considerable variation in intermediates from refinery to refinery but also within the same refinery over time.

In addition, in practice, a single intermediate stream storage tank may contain any number of different intermediate liquids that are destined for a particular downstream process or a set of possible processes.¹

Nevertheless, example composition and property information about intermediate streams along with hypothetical tank and tank control characteristics and turnover rates could be used to develop an assessment of the possible range of emissions from intermediate product storage tanks at refineries in Texas.

This report begins with a section on the characteristics of intermediate streams and the tanks that store them. Streams included are

- gas oils
- heavy and light naphthas

¹ For example, Hansen (2014) describes two tanks at refinery #14 whose contents are “Cat Crack Feed” with a material composition (volume %) of “High Sulfur, Catalytic Cracker Feed Mixture 100%; Heavy Gas Oil 0-100%; Vacuum Gas Oil 0-100%; Coker Gas Oil 0-100%; and Hydrogen Sulfide <0.04%.” Another tank whose contents are given as “Py Gas” has a material composition (volume %) of “Light Catalytic Cracked Petroleum Naphtha 0-100%; Heavy Catalytic Cracked Petroleum Naphtha 0-100%; Gasoline, Pyrolysis 0-100%; Debutanizer Bottoms 0-100%; Xylene 0-15%; Toluene 0-10%; and 1,2,4-Trimethylbenzene 0-7%.” Source: Hansen, S. August 20, 2014. Manager Environmental Affairs, Refinery #14. Personal communication (DIAL Tank Data).

- atmospheric and vacuum tower bottoms
- asphalt
- coker naphtha
- reformate
- pyrolysis gasoline
- residuum

Two Excel workbooks that collate data on the composition of the vapors from these streams and the composition of the liquid streams were prepared, as was an Excel workbook that collates data on physical property data for the streams.

The second section provides information about the common names for the liquid feedstocks and products of the following processes:

1. Isomerization unit
2. Catalytic reformer unit
3. Hydrocracker unit
4. Fluid catalytic cracking (FCC) unit
5. Alkylation unit
6. Hydrotreater unit
7. Hydrocracker unit

After that, information specific to refineries in Texas is described. These data are provided in several supplemental Excel workbook files. A discussion of methods for estimating emissions from storage tanks is next, followed by a section on cutter stock. The report ends with four appendices that provide crude oil assays, polyaromatic hydrocarbon (PAH) concentration in various refinery streams, speciated emissions from distillate oil storage tanks, and a discussion of possible discrepancies in the tank descriptions in the report for the TCEQ's differential absorption light detection and ranging (DIAL) study.

For ease of use, references are provided for each subsection of the report. However, in cases where references are not distinguishable by author and year alone, the letter used to distinguish the reference is maintained uniformly throughout the entire report in order to reduce confusion. The lettering conforms to the order of appearance in the first instance the references appear in the report.

NOTE: Many screenshots taken of figures and tables in the source documents are included in this report. Figure and table numbers included in the screenshots are meant to make it easier to find the data in the original source, not as numbering for tables and figures in this report.

Intermediate streams

The intermediate streams of particular interest in this report are 1) gas oils, 2) heavy and light naphtha, 3) atmospheric and vacuum bottoms, 4) asphalt, 5) coker naphtha, 6) reformate, 7) pyrolysis gasoline, and 8) residuum. Each of these streams is covered in a separate subsection in this section of the report.

There is no absolute agreement on which names are used for which streams at refineries, and the terms that get used can be confounding just because of the sheer number of possibilities. Some names are not useful without context. For example, refinery #14 reported a tank containing “recovery oil” and another tank holding “column tops” (Hansen 2014).

In some cases, a literature source, figure, or data table applies to more than one of the streams. Where this occurs, the source, figure, or data table is duplicated in order to make this report as useful as possible.

For each stream/stream category, literature for six areas of information was sought:

1. Stream origin(s) and destination(s):

Some of these streams are major distillation cuts. Others, sometimes in combination with streams that are major distillation cuts, are byproducts of upgrading or additional purification processes at refineries.

2. Physical properties

Data on the physical properties of intermediate streams was collected from sources that included facilities outside the US as well as US facilities. Available data provide an indication of the range of potential values.

Data about the physical properties of refinery intermediate storage tank liquids and vapors was collected and entered into an Excel workbook as part of this final report.

Supplementary Excel workbook: refinery intermediate storage tank liquid properties sanitized.xlsx

3. Composition of streams

As with intermediate stream properties, data on the composition of streams for refineries outside of the United States was collected along with composition data for streams at refineries in the United States. Available data illustrate possible compositions.

One Texas-specific source of data about the estimated emissions from refinery storage tanks holding intermediate streams is the US EPA’s refinery information collection request, which includes information from individual refineries about estimated emissions from storage tanks holding intermediates. These data, along with data from other sources, are collated into an Excel workbook that supplements this report:

Supplementary Excel workbook: refinery intermediate storage tank vapor composition sanitized.xlsx

Because the profile of chemicals in the vapor over a liquid mixture changes with temperature, this workbook includes information about temperature, where possible.

A similar collection of data on the composition of liquid intermediate streams is found in

Supplementary Excel workbook: refinery intermediate storage tank liquid composition.xlsx

4. Capacity, stocks, and throughput

The range of values for capacity, stocks, and throughput of intermediate stream storage tanks at refineries in Texas is described.

5. Storage tank characteristics

Storage tanks vary in size and shape, in the type of cover, and in the type of control systems. Fixed roof tanks have the highest emissions and are used only for low vapor pressure liquids. Internal floating roof tanks have lower emissions. Not all types of tanks are suitable for all types of products. Emission control methods on tanks range from no control to thermal oxidation of vapors with high destruction efficiency.

Useful formulas

Some correlations and unit conversions related to estimating properties needed in order to produce storage tank emission estimates and that apply to many or all of the streams in this section are discussed below.

Calculating the Watson characterization factor (K factor)

Drews (1998) provides the following formula for calculating a stream's K factor (this factor is a measure of the paraffinicity of petroleum fractions. This is also called the UOP K or UOPK factor. The formula for calculating the K factor is

$$K = \frac{\sqrt[3]{T_b}}{SG}$$

In this equation, K is the K factor, T_b is the normal boiling point of the liquid in °R, and SG is the specific gravity of the liquid at 60°F.

Converting API gravity to specific gravity at 60°F

API gravity is unitless but is often referred to as being in "degrees." It is a measure of the density of a liquid at 60°F relative to the density water at 60°F. A specific gravity of 1 at 60°F corresponds to 10° API. The formula for converting API gravity to specific gravity is

$$SG_{60^\circ F} = \frac{141.5}{131.5 + \text{API}}$$

In this equation $SG_{60^\circ F}$ is specific gravity at 60°F and API is API gravity.

Viscosity conversions

Sometimes viscosity of heavier streams is given in terms of Saybolt viscosity. Saybolt viscosity can be converted to dynamic or kinematic viscosity, as follows:

$$v_{SSU} = \frac{B\mu}{SG} = Bv_{\text{centistokes}}$$

where

v_{SSU} = Saybolt universal viscosity in Saybolt universal seconds (SSU); Saybolt Fural viscosity (v_{SSF}) is $0.1v_{SSU}$

$B = 4.632$ at 100°F (37.8°C)

$B = 4.664$ at 210°F (98.9°C)

μ = dynamic or absolute viscosity in centipoise (cP)

SG = specific gravity

$v_{\text{centistokes}}$ = kinematic viscosity in centistokes

Also,

$$\mu = v_{\text{centistokes}}SG = 0.001v_{\text{Pa-s}}$$

where $v_{\text{Pa-s}}$ = kinematic viscosity in Pa-s.

Correlations for estimating vapor pressure

Estimating vapor pressure at 100°F based on boiling point

Vapor pressure data are important for estimating emissions from storage tanks but are not always readily available. The following correlation estimates true vapor pressure at 100°F based on boiling point (Riazi et al 2003). That correlation is

$$\log(\text{TVP}_{100}) = 3.204 \left(1 - 4 \left(\frac{T_b - 41}{1393 - T_b} \right) \right)$$

In this equation, T_b is the normal boiling point in K and TVP_{100} is the true vapor pressure at 100°F (311 K) in bars.

Reid vapor pressure (RVP) is needed in order to apply one of the methods for calculating vapor pressure at various temperatures (US EPA, 2006a). A rough estimate of RVP can be made by ignoring the difference between Reid vapor pressure and true vapor pressure at 100°F (calculated using the above equation). It may be preferable to use the Maxwell-Bonnell correlations for estimating vapor pressure when normal boiling point and density, but not Reid vapor pressure, are available.

Estimating vapor pressure based on Reid vapor pressure and slope at 10 vol % evaporation

The American Petroleum Institute (API) (2012c with 2013 addendum) presents methods for calculating true vapor pressure for crude oils and refined petroleum stocks. There are two basic approaches for

estimating vapor pressure at different temperatures. The first method, suitable only for lighter (RVP 1-20 psi) refined streams whose distillation curves were developed using ASTM D-86, requires that the Reid vapor pressure and slope at 10 vol % evaporation be known. The second method relies on stream density (either specific gravity or API gravity) and true boiling point to estimate vapor pressure at various temperatures.

The following form of the Clausius-Clapeyron equation can be used for calculating true vapor pressure (API 2012c with 2013 addendum):

$$\ln P_{VA} = A - \frac{B}{T_{LA}}$$

In this equation, A is a dimensionless constant in the vapor pressure equation, B is a constant in °R in the vapor pressure equation, T_{LA} is the daily average liquid surface temperature in °R, and P_{VA} is the true vapor pressure at T_{LA} in pounds per square inch absolute (psia). If the vapor pressure is known for at least two temperatures, it is preferable to calculate A and B either via substitution or by linear regression instead of using the correlations presented in this section.

If the Reid vapor pressure of a refined petroleum stock is known and is between 1 and 20 psi, and the slope of the stock's distillation curve at 10% evaporation is known, the following equation can be used to find the vapor pressure of refined petroleum stocks (US EPA 2006a):

$$P = \exp \left\{ \left[0.7553 - \left(\frac{413.0}{T + 459.6} \right) \right] S^{0.5} \log_{10}(\text{RVP}) - \left[1.854 - \left(\frac{1,042}{T + 459.6} \right) \right] S^{0.5} + \left[\left(\frac{2,416}{T + 459.6} \right) - 2.013 \right] \log_{10}(\text{RVP}) - \left(\frac{8,742}{T + 459.6} \right) + 15.64 \right\}$$

Where:

- P = stock true vapor pressure, in pounds per square inch absolute.
- T = stock temperature, in degrees Fahrenheit.
- RVP = Reid vapor pressure, in pounds per square inch.
- S = slope of the ASTM distillation curve at 10 percent evaporated, in degrees Fahrenheit per percent.

Note: This equation was derived from a regression analysis of points read off Figure 7.1-14a over the full range of Reid vapor pressures, slopes of the ASTM distillation curve at 10 percent evaporated, and stock temperatures. In general, the equation yields P values that are within +0.05 pound per square inch absolute of the values obtained directly from the nomograph.

Figure 7.1-14b. Equation for true vapor pressure of refined petroleum stocks with a Reid vapor pressure of 1 to 20 pounds per square inch.⁴

This equation was developed for use with tanks holding refined petroleum stocks, but this is assumed to include intermediate streams as long as their Reid vapor pressure is 1-20 psi.

If the Reid vapor pressure is known and is between 1 and 20 psi and the stock distillation slope at 10 vol % evaporation is known, the Clausius-Clapeyron equation constants A and B can be calculated from (US EPA 2006a):

$$A = 15.64 - 1.854 S^{0.5} - (0.8742 - 0.3280 S^{0.5}) \ln(RVP)$$

$$B = 8.742 - 1.042 S^{0.5} - (1.049 - 179.4 S^{0.5}) \ln(RVP)$$

where:

RVP = stock Reid vapor pressure, in pounds per square inch
 ln = natural logarithm function
 S = stock ASTM-D86 distillation slope at 10 volume percent evaporation (°F/vol %)

Figure 7.1-15. Equations to determine vapor pressure constants A and B for refined petroleum stocks.⁸

Examples of stock distillation slopes at 10 vol % evaporation for gasoline (RVP 13, 10, and 7 psi), light naphtha (RVP 9-14 psi), naphtha (RVP 2-8 psi), and aviation gasoline are 3, 3.5, 2.5 and 2.0°F/vol % (API 2012 with 2013 addendum). The slope at 10% distillation can be found by taking the derivative of a curve that provides an appropriate fit to the data. While a systematic approach to developing values for the slope at 10 vol % evaporation is desirable, the behavior of the distillation curves around 10 vol % evaporation varies from distillation curve to distillation curve, and there is no hard and fast rule for which curve will best fit the data.

As shown in this table, it is probably adequate to use the slope of a linear fit to 3 data points that bracket 10 vol % evaporation:

Stream	Stock distillation slope at 10 vol % evaporation, °F/vol %			
	Thunder Horse crude based on ExxonMobil assay (not dated d)		HOOPS blend crude based on ExxonMobil assay (not dated c)	
	Based on derivative of best curve fit found by individual inspection	Based on linear fit of 5, 10, and 20 vol % values	Based on derivative of best curve fit found by individual inspection	Based on linear fit of 5, 10, and 20 vol % values
Light naphtha (C5- 165°F)	0.65	0.57	0.29	0.23
Heavy naphtha (165 - 330°F)	0.88	0.84	0.71	0.67
Kerosene (330 - 480°F)	0.52	0.50	0.47	0.45
Diesel (480 - 650°F)	0.53	0.52	0.57	0.56

The 10 vol % evaporation slopes reported in API (2012 with 2013 addendum) for gasoline, naphtha, and aviation gasoline are steeper than any of the slopes of the intermediate streams from the two assays. This may be because the API values are for finished products while the assays are meant to describe the straight run distillation streams (a type of intermediate product). All other things being equal, a smaller slope yields a lower vapor pressure (and a lower storage tank emission rate).

Estimating vapor pressure based on density and boiling point

If a stock's normal boiling point and API gravity (or specific gravity) are known, the true vapor pressure can be estimated using the Maxwell-Bonnell correlation (API 2012c with 2013 addendum Annex D). Jechura (2010) provides visual BASIC for applications (VBA) code that can be imported into Excel for calculating vapor pressures using the Maxwell-Bonnell correlation. The user must provide values for the temperature of interest (°F), the normal boiling point temperature (°F), and the K factor (unitless), in that order. If no K factor is specified, a default value of 12 is used. The Maxwell-Bonnell equations apply to petroleum fractions whose K factor is between 11.8 and 12.2 and whose boiling points are 38-371°C (100-700°F) (Drews 1998), but API (2012c with 2013 addendum) recommends them for low volatility stocks that the RVP/slope method does not apply to.

Predicting average molecular weight of a liquid

The molecular weight of petroleum fractions can be estimated if the 50% boiling point and the density are known (Goossens 1996). The equation is

$$MW = \frac{0.010770T_b^{1.52869+0.06486\ln\left(\frac{T_b}{1078-T_b}\right)}}{d}$$

In this equation, MW is molecular weight in g/mol, T_b is the normal boiling point of the petroleum fraction (or its 50 wt % total boiling point) in Kelvin, and d is the specific gravity of the fraction. This equation holds for streams containing C5-C120 with specific gravities from 0.63 to 1.08 and 50 wt % boiling points from 33-740°C. Note that as long as two of the three variables in the above equation are known, the third can be calculated.

Much of the time the distillation temperatures in crude assays are given in terms of volume % and not weight %. Volume % and weight% data taken for four distillation cuts (naphtha, kerosene, diesel, and gas oils) obtained from five different crudes (Stratiev et al 2011) indicate that the 50 volume % boiling point can be substituted for the 50 weight % boiling point.

This table provides a comparison of 50 weight % temperatures and 50 volume % temperatures from Stratiev and others (2011):

Crude	Temperature at 50% distillation, °C							
	Naphtha		Kerosine		Diesel		Gas oil	
	wt %	vol %	wt %	vol %	wt %	vol %	wt %	vol %
CPC	144	143	211	209	285	281	414	417
REBCO	145	143	214	211	301	297	441	441
Oil blend	146	143	214	212	303	298	441	440
SLCO	No data	No data	209	205	301	296	454	457
Kirkuk	144	143	209	206	306	301	448	448

Notes: CPC=a crude from Kazakhstan, Kirkuk is from Iraq, the oil blend is from Azerbaijan, SLCO=Siberian light crude oil from Russia, and REBCO=Russian export blend crude oil. Weight percent temperatures were obtained using ASTM D-2887 and volume percent temperatures were obtained using D-86/D-1160.

The volume percent and weight percent temperatures at distillation fractions away from 50% do not resemble each other the way the 50% temperatures do.

Correlation for predicting viscosity of heavy oils and asphalt at various temperatures

These correlations (Singh et al 1993) give good results for heavy oils and asphalts in the temperature range from 5-130°C. Comparisons between measured and calculated values are given by Singh and others (1993) and by Stratiev and others (2008).

When the viscosity at 30°C is known, the equations are:

$$\log(\mu) = B * \left[\frac{303.15}{(t + 273.15)} \right]^s - C$$

$$B = \log(\mu_o) + C$$

where $C = 3.0020$

$$s = 0.0066940 * B + 3.5364$$

$$= 0.0066940 * \log(\mu_o) + 3.5565$$

$$T_o = 303.15^\circ\text{K} (30^\circ\text{C})$$

$$t = \text{Prediction temperature, } ^\circ\text{C}$$

$$\mu_o = \text{measured viscosity, Pa} \cdot \text{s}$$

The parameter B is indicative of the viscosity of the particular material at 30°C and the parameter s is a measure of the variation of the viscosity with temperature. When the known viscosity is at a temperature other than 30°C, the viscosity at other temperatures can be estimated by using the BASIC program shown here (Singh et al 1993):

5 REM EQUATION LOG IS BASE 10 BUT PROGRAM LOG IS NATURAL LOGARITHM

10 SS=0.006694

20 IS=3.5364

```
30 C=3.002
40 INPUT "ENTER VISCOSITY, Pa-s:";VIST
50 INPUT "ENTER TEMPERATURE, DEGREES C:";TEMP
60 INPUT "ENTER TOLERANCE:";BTOL
70 BGUESS=0.6
80 AO=LOG(VIST)/LOG(10)
90 TQ=(TEMP+273.15)/303.15
100 AK=AO+C
110 P=LOG(TQ)
120 BNEW=BGUESS
130 BOLD=BNEW
140 Q=LOG(AK)
150 FB=LOG(BOLD)-SS*BOLD*P-(IS*P+Q)
160 FDER=1/BOLD-SS*P
170 BNEW=BOLD-FB/FDER
180 IF (ABS(BOLD-BNEW)>BTOL) THEN GOTO 130
190 PRINT
200 PRINT"B-";BNEW
210 B=BNEW:PRINT
220 INPUT "ENTER TEMPERATURE FOR PREDICTION, DEGREES C:";TEMP2
230 S=SS*B+IS
240 LVIS=B/((1+(TEMP2-30)/303.14)^S)-C
250 VIS=10^LVIS
260 PRINT
270 PRINT "PREDICTED VISCOSITY, Pa-s:";VIS
280 INPUT "PREDICT ANOTHER VISCOSITY (Y/N)?";A$
290 IF (A$="Y") THEN GOTO 220 ELSE END
```

Correlation for calculating true temperature at 50% distillation from ASTM D-86 temperature for 50% distillation

This formula is meant to convert the temperature at 50% distillation ($T_{50\%D-86}$) found using the ASTM D-86 method to the true temperature at 50% distillation ($T_{50\%}$) (Jechura 2014).

$$T_{50\%} = 0.87180T_{50\%D-86}^{1.0258}$$

A review of some of the assay data described later in this report shows that except for the butanes-and-lighter stream, the difference between $T_{50\%}$ and $T_{50\%D-86}$ when using this formula is generally going to be less than 3°F. It is unlikely that a correction of this magnitude is going to add to the uncertainty in estimated emissions, considering the large uncertainties in stream composition and other physical property data.

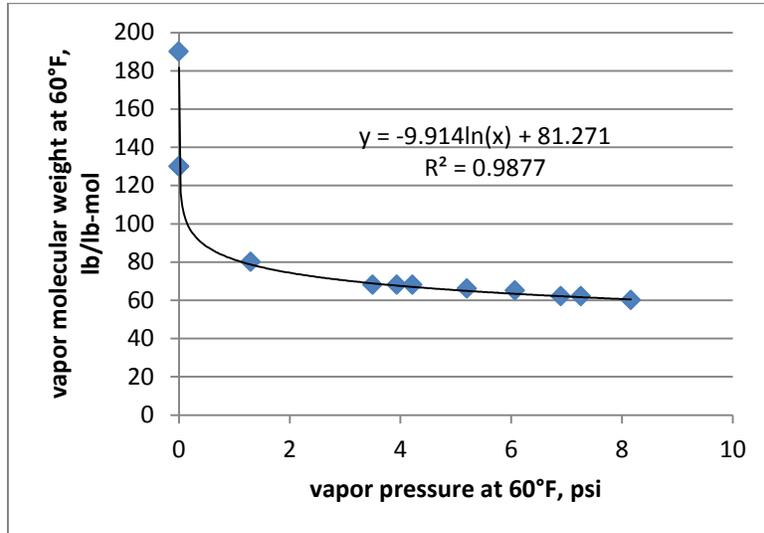
Estimating vapor molecular weight

Data on the molecular weight of vapor from intermediate streams is generally difficult to find, but this is one of the key data inputs for estimating and speciating emissions using the US EPA's TANKS Emissions Estimation Software, Version 4.09D software (US EPA 2006b) or the API (2012 with 2013 addendum) methods. The molecular weight of a vapor cannot be determined without knowing what the mole

fractions of all the components in the vapor phase are (API 2012 with 2013 addendum), and since mole fraction profiles have not been established for intermediate streams, this would require analysis of vapor samples.

The molecular weight of the vapor depends on temperature (rising with increasing temperature). A correlation for estimating vapor molecular weight from other stream properties could not be found.

For refined petroleum liquid mixtures, the molecular weight of the vapor at a given temperature appears to be related to vapor pressure, as shown in this figure:



The data points in this figure represent a broad range of streams, but only one of them (vacuum residual oil) is an intermediate stream, as shown in this table:

Liquid mixture	Molecular weight of vapor at 60°F	Vapor pressure at 60°F, psia	Calculated molecular weight of vapor based on correlation	% error in calculated molecular weight
Distillate fuel oil no. 2 ¹	130	0.0065	131	1%
Gasoline, RVP 7 ¹	68	3.5	69	1%
Gasoline, RVP 7.8 ¹	68	3.9363	68	0%
Gasoline, RVP 8.3 ¹	68	4.2188	67	1%
Gasoline, RVP 10 ¹	66	5.2	65	2%
Gasoline, RVP 11.5 ¹	65	6.069	63	3%
Gasoline, RVP 13 ¹	62	6.9	62	0.2%
Gasoline, RVP 13.5 ¹	62	7.2573	62	1%
Gasoline, RVP 15 ¹	60	8.1621	60	1%
Jet kerosene ¹	130	0.0085	129	1%
Jet naphtha (JP-4) ¹	80	1.3	79	2%
Fuel oil no. 6 ²	130	0.002	143	9%
Vacuum residual oil ²	190	0.00004	182	5%

¹From US EPA (2006a)

²From API (2012 with addendum dated 2013)

Data on vapor molecular weights at other temperatures are not readily available. The formula for the curve in the figure is only useful at 60°F (it is not even directionally correct for vapor pressures at other temperatures; it yields vapor molecular weights that are higher at lower temperatures and lower at higher temperatures).

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1. Gas oils

Material safety data sheets for refinery #10 (Refinery #10 2006a, b, c, d, e) list many synonyms for gas oils, as follows:

Vacuum gas oil: VGO, heavy vacuum gas oil, HVGO, heavy gas oil, heavy vacuum distillate, partially refined heavy gas oil, vacuum tower heavy gas oil from a petroleum crude still, vacuum tower sidestream, feedstock to the 634 hydrodesulfization (sic) unit, untreated FCCU feedstock, cracker unit feedstock, No. 6 fuel oil blending component, heavy fuel oil blending component, unfinished bunker fuel, C20-C50 petroleum hydrocarbons

Light gas oil: light vacuum gas oil (petroleum), LVGO, vacuum tower light gas oil, intermediate vacuum distillate, vacuum tower intermediate distillate, light paraffinic vacuum distillate, olefins plant feed – heavy, OPF-heavy, 634 HDS unit feed, 536 and 537 crude unit light vacuum gas oils, LGO stream from a vacuum still, untreated, unrefined, or raw No. 4 fuel oil, unfinished heavy heating oil, furnace oil, or burner fuel, C12-C30 petroleum hydrocarbons

Coker heavy gas oil: CHGO, delayed coker unit heavy gas oil, coker fractionator tower sidestream, cracked heavy gas oil, heavy gas oil from a thermocracker unit, thermal-cracked heavy gas oil, heavy thermocracked distillate, feedstock to the 634 hydrodesulfization (sic) unit, coker fractionator stripper tower bottoms, untreated FCCU feedstock, C15-C36 petroleum hydrocarbons

Light cycle oil: LCO, FCCU LCO, FCCU light cycle oil, fluid catalytic cracker unit light cycle oil, catalytic-cracked light gas oil, middle distillate cutter oil, untreated diesel fuel blending component, light catalytic cracked distillate (petroleum), C9-C25 petroleum hydrocarbons

Coker light gas oil: CLGO, coker LGO, medium distillate from a delayed coker unit, thermocracked light gas oil, light thermocracked distillate, light thermal cracked distillate (petroleum), thermal-cracked middle distillate, cracked middle distillate blending stock, C9-C22 petroleum hydrocarbons

According to these material safety data sheets, vacuum gas oil and coker heavy gas oil are in the “petroleum hydrocarbon heavy distillate” family, while light cycle oil, light gas oil, and coker light gas oil are in the “petroleum hydrocarbon middle distillate” or “petroleum hydrocarbon intermediate distillate” family.

Stream origins and destinations

The majority of gas oils produced at a refinery are direct distillation cuts. Atmospheric gas oil condenses in the lower portion of the atmospheric tower, while light vacuum gas oil and heavy vacuum gas oil are distillation cuts from vacuum distillation towers. Note that only two of the 23 refineries in Texas had no vacuum distillation as of January 1, 2014 (Koottungal 2013). These two refineries represented less than 2% of the total refining capacity in the state at that time.

Atmospheric gas oil can be sent to hydrocracking and/or catalytic cracking to create jet fuel and other fuels. The fraction between kerosene and lube oil is sometimes defined as gas oil and sometimes this fraction is divided into fractions named light gas oil and heavy gas oil. Sometimes the kerosene fraction

is lumped in with atmospheric distillation gas oils. Intermediates are the focus of this report, so the kerosene fraction of unfinished fuels is included as a gas oil in this section.

Gas oils can arise from separation steps for other refinery processes as well, such as coking, catalytic cracking, and hydrocracking; these streams are generally destined for the same processes as the atmospheric and vacuum distillation gas oils.

Vacuum gas oils can be sent to catalytic cracking, sometimes after hydrotreating to remove sulfur and nitrogen, to be converted into gasoline, jet fuel, or diesel. Heavy vacuum gas oil might be used as a flux oil in the manufacture of blown asphalt (Asphalt Institute Inc. and European Bitumen Association – Eurobitume 2011).

Physical properties of streams

Data available from the US EPA's refinery information collection request include the vapor pressure at the average storage tank temperature (along with that temperature) for "Unfinished Oils – Kerosene and light gas oils" and "Unfinished Oils – Heavy gas oils" in 129 storage tanks in Texas in the supplementary Excel workbook titled "component 1 intermediate storage tanks Texas with corrected tank ids with STARS heat info sanitized.xlsx." (STARS is the State of Texas Air Reporting System.) Refineries do not generally describe these streams in further detail and the instructions for the refinery information collection request do not provide guidance on how refineries were meant to distinguish between the various unfinished streams (for example, there is no guidance on what physical properties are used to distinguish between a light gas oil and a heavy gas oil). In addition, the sources and destinations of the streams are not described (in practice, storage tanks may contain gas oils from a mix of sources and/or be destined for a mix of downstream processes), so it is not generally possible to tell whether the data are for a tank storing a straight-run distillation cut or from a tank storing the gas oil output of a downstream processing step. It is clear from the data that some refineries categorized at last some of their processed gas oils and residuum in the "other" category of stream types.

Crude oil assays, which provide information about the expected products from distillation of various crudes, provide potentially useful information about the physical properties of distillation cuts like gas oils. The Energy Information Administration tracks information about crude imports by country for each Petroleum Administration for Defense (PAD) District but finer detail about the specific domestic and imported crude charges at refineries does not seem to be available, other than anecdotally with no reference for the source of information. In any case, data on the properties of major distillation cuts for any crude oil adds to an understanding of the potential range of properties of gas oils.

Appendix A describes supplementary Excel workbooks that contain assay data from ExxonMobil for two crudes fed to refineries in Texas (ExxonMobil not dated a, b): Hoover Offshore Oil Pipeline System (HOOPS) Blend (ExxonMobil not dated c) and Thunder Horse (ExxonMobil not dated d). These assays do not include some of the data that are useful for estimating storage tank emissions, like molecular weights or vapor pressures of the major distillation cuts.

An assay of Hibernia crude (Chevron 2011) is included in Appendix A because although this crude is not typically sold to Gulf Coast refineries, the assay provides an estimate for the molecular weight of the distillation cuts.

Another source of crude oil assays is Santos (not dated a, b, c, d, e). Santos is an energy services company operating in and around Australia and the crude oils it assayed are not expected to be utilized by Texas refineries. Their assays are included here because in some cases the Santos assays include vapor pressure and/or or molecular weights of the distillation cuts. The Santos assays and a more detailed description of the crude oils assayed are given in Appendix A.

The properties of coker gas oils at three refineries in China were analyzed by Hou et al (2007).

From Hou et al (2007):

Table 1. Property of the coker gas oil

Item	Coker gas oil		
	Daqing	Shengli	Liaohe
Density (70°) (g.cm ⁻³)	0.8308	0.8831	0.8575
Aniline point/°	94.7	76.4	82.2
Viscosity (50°) (mm ² .s ⁻¹)	11.7	12.95	11.67
Molecular weight	330	368	365
Refractive index (70°)	1.4647	1.4920	1.4972
Distillation range/°	210–489	213–507	243–534
ω[C], %	86.75	87.41	86.61
ω[H], %	12.79	12.45	12.65
ω[S], %	0.20	0.81	0.26
ω[N], %	0.23	0.55	0.51
ω[Ni]/(μg.g ⁻¹)	0.06	0.23	0.79
ω[V]/(μg.g ⁻¹)	0.03	0.06	0.06

Hou et al (2007) also described the properties of vacuum gas oil (despite the table heading, it is nearly a certainty that these data do not apply to coker gas oil):

Table 5. Property and composition of vacuum gas oil

Property and composition	Coker gas oil		
	Daqing	Shengli	Liaohe
Relative density (20°)	0.816	0.902	0.919
Formula weight	361	383	370
ω [carbon residue], %	0.15	0.27	0.95
ω [C], %	83.79	86.83	86.71
ω [H], %	15.67	12.29	12.70
ω [S], %	0.051	0.73	0.18
ω [N], %	0.072	0.14	0.41
Distillation range/ ^o	210–478	225–522	231–511
Content of group, %			
Alkane + naphthenone	83.72	72.42	76.30
Mononuclear aromatics	7.50	12.03	7.21
Bicyclic aromatics	3.22	3.47	3.30
Polycyclic aromatic hydrocarbon	4.50	8.30	11.60
Resin	1.06	3.78	3.31
The average structural parameters			
ω (C _A), %	11.05	14.53	17.91
ω (C _N), %	14.78	24.17	30.88
ω (C _P), %	73.17	61.30	51.21
R _A	0.51	0.58	0.96
R _N	0.83	1.53	2.13
R _T	1.34	2.11	3.09

The vacuum gas oil (HVGO) material safety data sheet (MSDS) for refinery #10 (Refinery #10 2006a) gives the boiling point range of this stream as 350-650°C (660-1,110°F) and the melting point range as 29-49°C (85-120°F). (Note that in spite of this melting point range, the MSDS characterizes this stream as a liquid.) The specific gravity at 60°F is 0.94-0.97. The vapor pressure is given as LT (less than) 0.1 Reid-*psia* at 38°C (100°F) and the viscosity is given as 195 to 500 cSt at 40°C.

The light gas oil (LVGO) MSDS for refinery #10 (Refinery #10 2006b) gives the boiling point range of this stream as 230-413°C (446-775°F) and the melting point range as 1-7°C (34-45°F). The specific gravity at 60°F is 0.88-0.90. The vapor pressure is given as 0.1 to 0.4 Reid-*psia* at 38°C (100°F) and the viscosity is given as 7.35 to 11.75 cSt at 40°C.

The coker heavy gas oil (CHGO) MSDS for refinery #10 (Refinery #10 2006c) gives the boiling point range of this stream as 260-510°C (500-950°F) and the melting point range as 24-43°C (75-110°F). The specific gravity at 60°F is 0.93-0.96. The vapor pressure is given as LT (less than) 0.1 Reid-*psia* at 38°C (100°F) and the viscosity is given as 150-325 cSt at 40°C.

The light cycle oil (FCCU) MSDS for refinery #10 (Refinery #10 2006d) gives the boiling point range of this stream as 150-415°C (302-780°F) and the melting point is LT (less than)-12°C (10°F). The specific gravity at 60°F is 0.94-0.95. The vapor pressure is given as 0.8-18 mm Hg at 20°C (68°F) or LT (less than) 0.1 Reid-psi at 38°C (100°F) and the viscosity is given as 3 to 7.5 cSt at 40°C.

The molecular weight of light catalytic cycle oil at refinery #3, whose emissions were estimated for the Texas Commission on Environmental Quality was 163 g/mol for vapor and 261 g/mol for liquid and the Reid vapor pressure was 0.06 psi (TCEQ 2010).

The coker light gas oil (CLGO) MSDS for refinery #10 (Refinery #10 2006e) gives the boiling point range of this stream as 140-370°C (285-700°F) and the melting point is <-15°C (<5°F). The specific gravity at 60°F is 0.84-0.88. The vapor pressure is given as < 0.1 Reid-psi at 38°C (100°F) and the viscosity is given as 3.65 to 7.35 cSt at 40°C.

A paper by Stratiev and others (2008) contains physical property information about 10 gas oil streams:

Property	SRGO 1	SRGO 2	SRGO 3	LCO	HCO	LVGO	HVGO 1	HVGO 2	HTVGO 1	HTVGO 2
Density at 20°C, g/cc	0.8008	0.8266	0.8533	0.942	0.992	0.8757	0.9189	0.9186	0.8901	0.8863
Distillation ASTM D-2887, °C										
IBP	84	114	183	139	198	196	314	250	298	287
5%	141	194	244	189	248	247	349	362	346	342
10%	163	213	260	206	257	263	365	380	364	360
30%	194	238	288	230	287	297	409	409	403	400
50%	208	254	309	251	309	317	443	437	433	429
70%	222	267	331	269	331	337	478	467	464	461
90%	243	287	361	294	362	363	517	503	506	504
95%	253	297	373	304	378	375	529	524	521	520
FBP	273	327	402	339	416	406	543	544	542	541
Molecular weight,* g/mol	155	185	227	160	195	229	363	354	359	356
Refraction, nD20	1.4463	1.4612	1.4755	1.5533	1.5883	1.4891	1.5184	1.5138	1.5007	1.5
Temperature, °C.	Viscosity, sq mm/sec									
20	1.8	3.25	8.45	3.08	11.1	10.4				
30	1.52	2.62	6.11	2.49	8.25	7.49				
40	1.32	2.16	4.71	2.01	5.46	5.62	44.3	64.3		
50	1.16	1.84	3.75	1.71	4.46	4.36	25.7	37.5	28.8	25.6
60	1.03	1.58	3.05	1.45	3.29	3.47	16	24.4	19.6	17.7
70							10.8	17.0	14.07	13.51
80							7.75	12.4	10.4	9.57

*Stratiev and others (2008) report that this value was estimated using Goossens 1993. Notes: SRGO=straight run gas oil; LCO=light cycle oil (FCC); HCO=heavy cycle oil (FCC); LVGO=light vacuum gas oil; HVGO=heavy vacuum gas oil; HTVGO=hydrotreated heavy vacuum gas oil.

API (2012 with 2013 addendum) reports the following properties for vacuum residual oil:

Property	Value
Vapor molecular weight, lb/lb-mole	190
Liquid molecular weight, lb/lb-mole	387
Condensed vapor density at 60°F, lb/gal	6.4
Liquid density, lb/gal	7.9
Estimated Clausius-Clapeyron equation constant A, dimensionless	10.104
Estimated Clausius-Clapeyron equation constant B, °R	10,475.5
Vapor pressure at 60°F, psia*	0.00004

*Calculated from estimated Clausius-Clapeyron equation constants

Some physical property data for straight-run kerosene is given here (US EPA 2003):

Property	Sample API 83-09
CAS number	8008-20-6
Pour point (°C)	-49
Density (kg/dm ³)@ 15 °C	0.81
Reid vapor pressure @ 37.8 °C (hPa)	14
Flash point (closed cup) °C	62
Kinematic viscosity at 20 °C (mm ² /sec)	1.5-2.5
Gravity (°API)	43.0
Sulfur (wt %)	0.47
Nitrogen (ppm)	5.4
Flash point (°F)	144
Distillation (°F)	
IBP	238
10%	327
50%	405
90%	475
95%	490
EP	520
Paraffins (%)	-
Saturates (%)	82
Olefins (%)	2.5
Naphthenes (%)	-
Aromatics (%)	15.5

Elsewhere in US EPA (2003), the vapor pressure of straight-run kerosene is given as 1.4 kPa at 37.8°C and the boiling point range is given as 125-292°C, and the boiling point range of a hydrocracked heavy aromatic kerosene is given as 187-288°C.

Composition of streams

The Thunder Horse and HOOPS blend assays described earlier (as well as the non-Texas fed assays) have a breakdown of hydrocarbon types (paraffins, naphthenes, aromatics) for the gas oil cuts. For the gas oils, the fractional values for these three categories do not add up to 100%, perhaps because they do not include compounds with nitrogen or sulfur. These assays also have the fraction of naphthalenes in the kerosene cut. More information about these assays (along with other assays that contain this type of information for crude oils not fed to Texas refineries) is given in Appendix A of this report).

Table 5 from Hou et al (2007) (see above) has a breakdown of compound groups found in vacuum gas oils at 3 refineries in China. It is impossible to tell from the writeup whether these are by mass or by volume.

Hou et al (2007) provides a breakdown of compound groups found in coker gas oil at 3 refineries in China:

Table 2. Content of five group fractions of coker gas oils

Content of group	Coker gas oil		
	Daqing	Shengli	Liaohe
Saturated hydrocarbon	68.3	55.1	60.9
Light aromatics	7.9	13.6	5.2
Medium aromatics	4.2	8.8	6.5
Heavy aromatics	12.7	15.0	21.5
Resin	6.9	11.5	5.7

As with the previous table, the Hou et al (2007) paper does not specify whether these are by mass or by volume.

A more detailed breakdown of compounds found in the coker gas oil at three refineries in China is also given in Hou et al (2007):

Table 3. Content of hydrocarbon of coker gas oils (¹H-NMR) %

Content of hydrocarbon	Coker gas oil		
	Daqing	Shengli	Liaohe
Paraffintic hydrocarbon	35.1	20.8	27.5
Total naphthenone	32.3	33.1	33.9
Mononuclear naphthenone	17.7	7.8	10.9
Bicyclonaphthenone	8.0	8.1	8.4
Tricyclonaphthenone	3.3	11.2	6.9
Tetracyclonaphthenone	3.3	4.5	5.1
Pentanuclear naphthenone	0	1.5	2.6
Hexacyclic ring naphthenone	0	0.3	0
Total aromatic	26.7	33.3	30.1
Total mononuclear aromatics	7.9	4.6	3.2
Alkylbenzene	3.7	2.2	0.8
Naphthene base alkylbenzene	2.1	1.5	0.9
Bicyclonaphene base alkylbenzene	2.1	0.9	1.5
Total bicyclic aromatics	7.4	4.4	3.6
Naphthalene group	1.9	0	0
Acenaphthene group + diphenylene-oxide	2.2	2.8	1.5
Fluorene group	3.3	1.6	2.1
Total triaromatics	5.6	5.0	5.9
Phenanthrene group	3.4	3.1	3.1
Cycloalkane naphthene phenanthrene group	2.2	1.9	2.8
Total tetranuclear	4.3	10.7	11.0
Pyrene group	3.1	5.7	5.9
Chrysene group	1.2	5.0	5.1
Total pentanuclear aromatics	0.4	3.9	2.3
Pyrene group	0.4	3.9	2.3
Dibenzanthracene	0	0	0
Total thiophene	1.0	3.2	2.7
Benzothiophene	0.4	1.7	0.7
Dibenzothiophene	0.4	1.1	0.6
Thiophanthrene	0.2	0.4	0.4
Unappraisal aromatic	1.1	1.5	1.4
Resin	6.9	12.8	8.5

A gas chromatography-mass spectroscopy (GC-MS) analysis of the compounds in a partially hydrogenated vacuum gas oil is given in Moustafa and Froment (2003):

Table 2. Composition of HVGO (wt %)

no. of C	nPAR	iPAR	MNA	DNA	TNA	QNA	MAR	DAR	TAR	NMA	NDA	NTA	sum
14							0.827	0.047		0.413			1.287
15	0.002						2.33	0.359			0.18		2.871
16	0.016	0.002	0.004				2.71	1.01			0.5		4.242
17	0.077	0.002	0.032	0.021			2.32	0.95	0.323		0.47		4.195
18	0.167	0.039	0.128	0.131	0.022		1.61	0.915	0.459			0.23	3.703
19	0.365	0.152	0.339	0.312	0.109	0.018	0.718	0.335	0.126			0.063	2.537
20	0.729	0.333	0.614	0.613	0.247	0.196	0.246	0.168	0.078			0.039	3.263
21	1.01	0.57	1.03	1.05	0.541	0.447	0.086	0.113	0.047			0.023	4.917
22	1.43	0.91	1.47	1.38	0.65	0.723	0.012	0.02	0.01				6.605
23	1.56	1.27	1.92	1.77	0.873	0.793							8.186
24	1.86	1.6	2.38	2.22	1.24	0.873							10.17
25	2.07	1.72	2.79	2.46	1.37	0.693							11.1
26	1.65	1.45	2.59	2.27	1.09	0.533							9.583
27	1.27	1.36	2.38	2.11	0.897	0.439							8.456
28	0.9	1.11	2.07	1.93	0.615	0.395							7.02
29	0.538	0.723	1.55	1.52	0.403	0.235							4.969
30	0.343	0.426	1.15	1.14	0.163	0.118							3.34
31	0.183	0.268	0.712	0.608	0.09	0.082							1.943
32	0.115	0.163	0.405	1.248	0.092	0.06							1.083
33	0.04	0.07	0.236	0.015	0.125	0.047							0.533
sum	14.3	12.2	21.8	19.8	8.52	5.65	10.89	3.917	1.045	0.413	1.15	0.355	100

In this table, nPAR is normal paraffins, iPAR is isoparaffins, MNA is mononaphthenes, DNA is dinaphthenes, TNA is trinaphthenes, QNA is tetranaphthenes, MAR is mono-aromatics, DAR is di-aromatics, TAR is tri-aromatics, NMA is naphtheno-mono-aromatics, NDA is naphtheno-di-aromatics, and NTA is naphtheno-tri-aromatics.

In 2001, the Canadian Petroleum Products Institute (CPPI) analyzed a number of refinery streams for polycyclic aromatic hydrocarbons (PAHs). The results for gas oil streams are given in Appendix B.

US EPA's SPECIATE 4.4 database (US EPA 2014a) contains a composite speciation of emissions from 9 tanks storing distillate oils from a study done in the early 1990s. While this study is ubiquitously referenced and the data were being used to draft air emission permits as recently as 2013 (Minnesota Pollution Control Agency 2013), the original work was not found. It is possible that the tanks whose data were composited for SPECIATE were a combination of naphtha and gas oil tanks. The speciation data can be found in Appendix C. Nearly 30% of the emissions are attributed to n-butane and another nearly 30% are unidentified. It is important to remember that speciation in the vapor over a liquid mixture varies with temperature; temperatures were not provided in the SPECIATE data.

The MSDS for vacuum gas oil at refinery #10 (Refinery #10 2006a) says that its vacuum gas oil (HVGO) is 85-95% saturated hydrocarbons and naphthenes and 5-15% polynuclear aromatic hydrocarbons (4- to 6-member condensed-ring type²). The list of compounds found in the workplace exposure section of this MSDS may provide clues about the compounds present in the stream. This list is: hydrogen sulfide; oil mist, mineral; coal tar pitch volatiles, as benzene solubles ("A1" confirmed human carcinogen); and oil

² Condensed aromatic rings (also called fused ring systems) have carbon atoms in their aromatic rings that are shared by two or three aromatic rings. A 4- to 6-member condensed-ring type polynuclear aromatic hydrocarbon has four to six aromatic rings, each of which shares at least two of its carbon atoms with at least one other aromatic ring.

mist, mineral, sum total of 15 PAHs listed as carcinogens by US NTP. (Note that the 15 PAHs listed by US NTP (2011) are benz[a]anthracene, benzo[b]fluoranthene, benzo[j]-fluoranthene, benzo[a]pyrene, dibenz[a,h]acridine, dibenz[a,j]acridine, dibenz[a,h]anthracene, 7H-dibenzo[c,g]-carbazole, dibenzo[a,h]pyrene, dibenzo[a,i]pyrene, indeno[1,2,3-cd]pyrene, benzo[k]fluoranthene, dibenzo[a,e]pyrene, dibenzo[a,l]pyrene, and 5-methylchrysene.) Under “volatile characteristics,” this MSDS says “Negligible; no Volatile Organic Compounds (VOCs) present at 500°F (260°C).”

The MSDS for light gas oil (LVGO) at refinery #10 (Refinery #10 2006b) says that its light gas oil is 0-1.5% biphenyl, 59-80% C13-C30 saturated hydrocarbons and naphthenes, 20-40% C13-C30 aromatic hydrocarbons, and 0.1-5% polynuclear aromatic hydrocarbons (4- to 6-member condensed-ring type). The list of compounds found in the workplace exposure section of this MSDS may provide clues about the compounds present in the stream. This list is: diesel fuel/kerosene (“A3” animal carcinogen); biphenyl; oil mist, mineral; coal tar pitch volatiles, as benzene solubles (“A1” confirmed human carcinogen); and oil mist, mineral, sum total of 15 PAHs listed as carcinogens by US NTP. (Note that the 15 PAHs listed by US NTP (2011) are benz[a]anthracene, benzo[b]fluoranthene, benzo[j]-fluoranthene, benzo[a]pyrene, dibenz[a,h]acridine, dibenz[a,j]acridine, dibenz[a,h]anthracene, 7H-dibenzo[c,g]-carbazole, dibenzo[a,h]pyrene, dibenzo[a,i]pyrene, indeno[1,2,3-cd]pyrene, benzo[k]fluoranthene, dibenzo[a,e]pyrene, dibenzo[a,l]pyrene, and 5-methylchrysene.) Under “volatile characteristics,” this MSDS says “Slight, no Volatile Organic Compounds (VOCs) present at 400°F (204°C).”

The MSDS for coker heavy gas oil (CHGO) at refinery #10 (Refinery #10 2006c) says that its coker heavy gas oil is 75-90% C15-C36 saturated hydrocarbons and naphthenes and 10-25% polynuclear aromatic hydrocarbons (4- to 6-member condensed-ring type). The list of compounds found in the workplace exposure section of this MSDS may provide clues about the compounds present in the stream. This list is: hydrogen sulfide; oil mist, mineral; coal tar pitch volatiles, as benzene solubles (“A1” confirmed human carcinogen); and oil mist, mineral, sum total of 15 PAHs listed as carcinogens by US NTP. (Note that the 15 PAHs listed by US NTP (2011) are benz[a]anthracene, benzo[b]fluoranthene, benzo[j]-fluoranthene, benzo[a]pyrene, dibenz[a,h]acridine, dibenz[a,j]acridine, dibenz[a,h]anthracene, 7H-dibenzo[c,g]-carbazole, dibenzo[a,h]pyrene, dibenzo[a,i]pyrene, indeno[1,2,3-cd]pyrene, benzo[k]fluoranthene, dibenzo[a,e]pyrene, dibenzo[a,l]pyrene, and 5-methylchrysene.) Under “volatile characteristics,” this MSDS says “Negligible, no Volatile Organic Compounds (VOCs) present at 450°F (232°C).”

The MSDS for light cycle oil (presumably from the FCCU) at refinery #10 (Refinery #10 2006d) says that its light cycle oil stream is 1-10% nonanes, 0.5-1.5% trimethylbenzene (mixed isomers); 1-3% ethylmethylbenzenes; 25-35% C10-C12 alkanes, isoparaffins, cycloalkanes, and naphthenes; 1-3% naphthalene; 5-15% C10-C11 alkylbenzenes; 5-10% C10-C16 alkene hydrocarbons; 1-5% biphenyl; 5-15% C12-C23 aromatic hydrocarbons; 0.1-1 polynuclear aromatic hydrocarbons (4- to 6-member condensed-ring type); 15-35% C13-C25 alkanes, isoparaffins, cycloalkanes, and naphthenes; and 1-10% C17-C24 alkene hydrocarbons. (Note that this list of constituents does not necessarily include all compounds in the stream.) The list of compounds found in the workplace exposure section of this MSDS may provide clues about the compounds present in the stream. This list is: diesel fuel/kerosene (“A3” animal

carcinogen); nonane, all isomers; trimethylbenzene (mixed isomers); naphthalene (“A4” = not classifiable); biphenyl, coal tar pitch volatiles, as benzene solubles (“A1” confirmed human carcinogen); and diesel exhaust, particulate aerodynamic diameter < 1 µm (“A2” suspected human carcinogen). Under “volatile characteristics,” this MSDS says “Volatile Organic Compounds (VOCs) content = 30% below 400°F, 825-925 mg/L.”

The MSDS for coker light gas oil at refinery #10 (Refinery #10 2006e) says that its coker light gas oil stream is 0-1.5% xylenes (mixed isomers); 0.5-1.5% trimethylbenzene (mixed isomers); 0.5-2% ethylmethylbenzenes; 1-3% naphthalene; 1-5% C10-C11 alkylbenzenes; 15-25% C11 alkanes, isoparaffins, cycloalkanes, and naphthenes; 20-40% C12 alkanes, isoparaffins, cycloalkanes, and naphthenes; 1-5% biphenyl; 10-20% C12-C21 aromatic hydrocarbons; 20-35% C13-C22 alkanes, isoparaffins, cycloalkanes, and naphthenes; and 0.1-1% polynuclear aromatic hydrocarbons (4- to 6-member condensed-ring type). (Note that this list of constituents does not necessarily include all compounds in the stream.) The list of compounds found in the workplace exposure section of this MSDS may provide clues about the compounds present in the stream. This list is: diesel fuel/kerosene (“A3” animal carcinogen); xylenes (mixed isomers); trimethylbenzene (mixed isomers); naphthalene; biphenyl; and coal tar pitch volatiles, as benzene solubles. Under “volatile characteristics,” this MSDS says “Slight, some Volatile Organic Compounds (VOCs) present at 302°F (150°C).”

A paper by Stratiev and others (2008) contains composition information about 10 gas oil streams that are relevant to Texas refineries:

Property	SRGO 1	SRGO 2	SRGO 3	LCO	HCO	LVGO	HVGO 1	HVGO 2	HTVGO 1	HTVGO 2
Composition, %										
Saturates	79	73.4	71	13	19.2	64		51	59	
Monoaromatics	15	18.1	17.2	36	27.8	20.3		18	22.4	
Polyaromatics	6	8.5	11.8	51	53	15.7		29	17.9	
Olefins										
Resins								2	0.7	
Asphaltenes										
Sulfur, %	0.2	0.4	0.85	0.05	0.2	1.2	1.6	1.6	0.08	0.08
Hydrogen, % (estimated using a correlation)	13.9	13.5	13.2	8.7	78	12.6	11.8	12.1	12.5	12.5

Notes: SRGO=straight run gas oil; LCO=light cycle oil; HCO=heavy cycle oil; LVGO=light vacuum gas oil; HVGO=heavy vacuum gas oil; HTHVGO=hydrotreated heavy vacuum gas oil.

Capacity, stocks, and throughput

The US EPA’s refinery information collection request (US EPA not dated) asked for the volume produced in 2010 of gas oil streams including “Unfinished Oils – Kerosene and light gas oils” and “Unfinished Oils – Heavy gas oils.” These values are given in the “products produced” worksheet of the supplementary Excel workbook titled “component 1 Texas refinery details sanitized.xlsx.” However, many of the quantity fields are blank, presumably because they were confidential business information.

Twenty-one refineries list “Unfinished Oils – Kerosene and light gas oils” as a product but only two provide an annual production value: refinery #xxx reports production in 2010 of 115,334 bbl and refinery #13 reports production in 2010 of 9,441,000 bbl. Eight of the 21 refineries in this group provided information about whether this stream was used onsite or transferred offsite. Four refineries (#xxx, #6, #12, and #11) report that none of the “Unfinished Oils – Kerosene and light gas oils” they produce are used onsite, while another two refineries (#7 and #19) report that 100% of this stream is used onsite. The remaining two refineries (#13 and #8), report 10% and 14% onsite usage, respectively.

Nineteen refineries list “Unfinished Oils – Heavy gas oils” as a product. The same two refineries that provided annual production of the kerosene and light gas oils are the only two that provide an annual production value for “Unfinished Oils – Heavy gas oils:” refinery #xxx reports production in 2010 of 256,548 bbl and refinery #13 reports production in 2010 of 1,914,000 bbl. Eight of the 19 refineries in this group provided information about whether this stream was used onsite or transferred offsite. Three refineries (#6, #7, and #11) report that none of the “Unfinished Oils – Heavy gas oils” they produce are used onsite, while another two refineries (#4b and #19) report that 100% of this stream is used onsite. The remaining three refineries (#13, #xxx, and #8), report 0.06%, 9% and 80% onsite usage, respectively.

The US EPA’s refinery information collection request (US EPA not dated) also includes data on throughput by tank. The supplementary Excel workbook titled “component 1 intermediate storage tanks Texas with corrected tank ids with STARS heat info sanitized.xlsx” includes information about storage tanks at refineries in Texas holding “Unfinished Oils – Kerosene and light gas oils” and “Unfinished Oils – Heavy gas oils.” Many of the streams in the “other” category are also gas oil streams. A total of 140 tanks were reported to be holding gas oils (note that in a few cases some interpretation was required when determining which tanks held gas oils).

Reported throughput volumes vary widely amongst the stream categories. Average, maximum, and minimum throughputs for each of the gas oil stream categories are given in the table below.

Stream category	Throughput per tank in 2009, bbl				number of tanks in sample
	average	standard deviation	max	min	
Unfinished Oils – Kerosene and light gas oils	1,193,969	1,598,131	5,410,710	0	20
Unfinished Oils – Heavy gas oils	2,374,732	2,526,307	8,330,586	0	19
PDA* Gasoil Charge	120,000	n/a	n/a	n/a	1
Unfinished Diesel	2,625,829	949,263	3,297,059	1,954,598	2
Cutter stock	184,731	n/a	n/a	n/a	1
FCCU Feed	2,250,635	2,877,453	5,494,955	7,567	3
Gas Oil (FCCU)	2,465,671	3,254,469	4,766,928	164,414	2
MDH* Feed	929,511	312,050	1,150,164	708,858	2

*These acronyms are not spelled out in the refinery information collection request data, but PDA probably stands for propane deasphalting and MDH probably stands for mixed-distillate hydrotreating.

Note that some tanks were reported to have a throughput of 0 and that throughput is only available for 50 of the 140 tanks holding gas oils.

While individual refineries vary considerably in their configuration, the feed capacity for catalytic cracking and for processes identified as distillate upgrading might help to provide a sense of the potential volume of the production of heavy gas oils.

Information about process capacities is contained in two of the supplementary Excel workbooks described in the section titled "Refineries in Texas." One source of capacity information is data collected from US EPA's refinery information collection request (US EPA not dated) and can be found in the "processes at refineries" worksheet in the "component 1 Texas refinery details sanitized.xlsx" workbook. Refineries in this workbook are identified by number.

Data from Koottungal (2013) were used to create another supplementary Excel workbook that gives charge capacities for many processes including catalytic cracking and hydrocracking charge capacities as of January 1, 2014. The refineries in this workbook are identified by number and by region (inland or Gulf Coast).

This table shows the values for catalytic cracking and catalytic hydrocracking from both sets of data.

refinery #	Capacity in barrels per calendar day					
	Koottungal 2013 (values as of Jan 1, 2014)			US EPA not dated (values for 2010)		
	catalytic cracking	distillate catalytic hydrocracking	total catalytic cracking and distillate catalytic hydrocracking	fluid catalytic cracking unit ¹	catalytic hydrocracking ²	total catalytic cracking and catalytic hydrocracking
1	0	0	0	0	0	0
2	24,000	0	24,000	24,000		24,000
3	163,900	65,600	163,900	CBI	CBI	CBI
4	72,450	0	72,450	84,493		84,493
5	97,000	0	97,000	111,246		111,246
6	20,200	0	20,200	20,000		20,000
7	204,500	26,500	204,500	CBI	CBI	CBI
8	113,000	60,000	113,000	CBI	CBI	CBI
9	94,230	11,700	94,230	106,700	13,000	119,700
10	97,000	0	97,000	105,000		105,000
11	56,000	0	56,000	55,600		55,600
12	88,000	0	88,000	88,000		88,000
13	50,000	0	50,000	CBI		CBI
14	66,300	53,400	66,300	70,000	60,000	130,000
15	74,772	0	74,772	85,000		85,000
16	92,000	49,000	92,000	93,100	51,100	144,200
17	67,000	34,000	67,000	65,000		65,000
18	80,000	0	80,000	78,600	45,000	123,600
19	54,465	0	54,465	54,500	30,000	84,500
20	80,000	0	80,000	83,500		83,500
21	24,500	0	24,500	25,000	30,000	55,000
22	28,000	0	28,000	35,000		35,000
23	55,000	0	55,000	59,000		59,000
xxx				0	0	0
Total all	1,702,317	300,200	2,002,517	³	³	³

Notes: CBI=confidential business information

¹All of the reported values were for fluid catalytic cracking units (no refinery reported non-fluid catalytic cracking units) in US EPA (not dated). Refineries were instructed to include recycle when reporting the values in this column; in contrast, Koottungal (2013) is silent about whether recycle is included in the catalytic cracker capacities.

² The values in this column are for all hydrocracking, not just distillate hydrocracking. Koottungal (2013) found that two-thirds of the catalytic hydrocracking capacity statewide was for distillate upgrading.

³No totals are given here because they would be distorted by the missing information from refineries with confidential business information claims.

Refinery #13 is the only refinery that provided production volumes for gas oils in the refinery information collection request and that appears in the above table. Koottungal's (2013) value for

catalytic cracker capacity is 50,000 barrels per calendar day (or 18,250,000 barrels per year), and per the information collection request (US EPA not dated), gas oil production at this refinery was 11,355,000 bbl in 2010. This refinery also reported that they use 10% of their kerosene and light gas oils and 0.6% of their heavy gas oils onsite. For this refinery, therefore, the catalytic cracking and hydrocracking capacity is incongruous with the reported amount produced.

Data about the month-to-month change in stored quantities of intermediate gas oils may shed light on tank turnover rates as well. The US Energy Information Administration (US EIA) tracks information about refinery stocks of unfinished oils characterized as “kerosene and light oils” and “heavy gas oils.” US EIA data for Texas is divided into Gulf Coast and inland refineries (individual refinery data is not published). The following table shows the most recent 12 months of data. US EIA defines “unfinished oils” as all oils requiring further processing, except those requiring only mechanical blending. Kerosene is defined as having a maximum distillation temperature of 400°Fahrenheit at the 10-percent recovery point and a final boiling point of 572°Fahrenheit; heavy gas oils are defined as those having an approximate boiling range from 651°F to 1000°F. Light oils are not specifically defined but would presumably have higher boiling points than naphthas; US EIA defines “naphtha” as a petroleum fraction with an approximate boiling range of 122-400° F (US EIA not dated).

Stocks of Kerosene and Light Oils and Stocks of Heavy Gas Oils at Refineries in Texas

Date	Refining District Texas Inland Kerosene and Light Oils Stocks at Refineries (Thousand Barrels) ¹	Refining District Texas Gulf Coast Kerosene and Light Oils Stocks at Refineries (Thousand Barrels) ¹	Refining District Texas Inland Heavy Gas Oils Stocks at Refineries (Thousand Barrels) ²	Refining District Texas Gulf Coast Heavy Gas Oils Stocks at Refineries (Thousand Barrels) ²
May-2013	590	4,580	473	8,558
Jun-2013	428	5,023	459	8,104
Jul-2013	418	4,486	328	8,689
Aug-2013	335	4,091	314	8,873
Sep-2013	365	4,377	436	9,148
Oct-2013	416	4,419	440	9,783
Nov-2013	401	4,189	405	8,866
Dec-2013	510	3,908	426	7,477
Jan-2014	569	4,624	430	8,066
Feb-2014	1,034	4,096	578	8,429
Mar-2014	808	4,408	305	9,007
Apr-2014	767	4,233	434	9,764

¹From US EIA, June 27, 2014i

²From US EIA, June 27, 2014j

Storage tank characteristics

Detailed information about storage tanks holding intermediates was obtained during the US EPA’s refinery information collection request (US EPA not dated). The supplementary Excel workbook titled “component 1 intermediate storage tanks Texas with corrected tank ids with STARS heat info sanitized.xlsx” includes information about storage tanks at refineries in Texas holding “Unfinished Oils – Kerosene and light gas oils” and “Unfinished Oils – Heavy gas oils.” Many of the streams in the “other” category are also gas oil streams. Data include the type of tank, dimensions, average storage temperature, types of rim seals, how many times the roof was landed (for floating roof tanks) and what type of controls were used the last time the tank was degassed. This information may reveal whether the same tank was used for more than one product. There is no information about insulation or type of heater used for heated tanks.

A total of 140 tanks were reported to be holding gas oils (note that in a few cases some interpretation was required when determining which tanks held gas oils). Tank types for each stream category are given in the following table.

Stream category	Number of tanks				
	Fixed roof tank vented to atmosphere	External floating roof	Internal floating roof	Cone roof tanks	Total
Unfinished Oils – Kerosene and light gas oils	34	9	5	6	54
Unfinished Oils – Heavy gas oils	70	5			75
PDA* Gasoil Charge	1				1
Unfinished Diesel	2				2
Cutter stock				1	1
FCCU Feed	3				3
Gas Oil (FCCU)	2				2
MDH* Feed			2		2

*These acronyms are not spelled out in the refinery information collection request data, but PDA probably stands for propane deasphalting and MDH probably stands for mixed-distillate hydrotreating.

Tank sizes vary widely amongst the different stream categories, except for MDH feed, which was only reported for two tanks at a single refinery. Average, maximum, and minimum tank sizes for each of the stream categories are given in the table below.

Stream category	Number of tanks in sample	Tank capacity, ft ³			
		average	standard deviation	max	min
Unfinished Oils – Kerosene and light gas oils	45	342,797	304,285	1,507,200	4,916
Unfinished Oils – Heavy gas oils	74	500,337	504,763	2,151,115	3,020
PDA* Gasoil Charge	0	Maximum liquid height not given for any tanks			
Unfinished Diesel	2	621,974	269,409	812,475	431,474
Cutter stock	0	Maximum liquid height not given for any tanks			
FCCU Feed	3	586,380	607,836	1,231,591	24,521
Gas Oil (FCCU)	0	Maximum liquid height not given for any tanks			
MDH* Feed	2	175,371	146	175,474	175,268

*These acronyms are not spelled out in the refinery information collection request data, but PDA probably stands for propane deasphalting and MDH probably stands for mixed-distillate hydrotreating.

For the 36 gas oil tanks with both capacity and throughput data, the average throughput:capacity ratio was 4.6 bbl of throughput/ft³ of capacity (standard deviation of 6.9 bbl of throughput/ft³ of capacity).

Reported temperatures amongst the stream categories are more uniform than capacity. Average, maximum, and minimum temperatures for each of the stream categories are given in the table below.

Stream category	Temperature, °F				number of tanks in sample
	average	standard deviation	max	min	
Unfinished Oils – Kerosene and light gas oils	94	28	191	62	54
Unfinished Oils – Heavy gas oils	137	80	480	54	70
PDA Gasoil Charge	177	n/a	n/a	n/a	1
Unfinished Diesel	90	3	92	87	2
Cutter stock	177	n/a	n/a	n/a	1
FCCU Feed	153	35	177	113	3
Gas Oil (FCCU)	200	0	200	200	2
MDH Feed	118	4	120	115	2

*These acronyms are not spelled out in the refinery information collection request data, but PDA probably stands for propane deasphalting and MDH probably stands for mixed-distillate hydrotreating.

Detailed information used to develop emission estimates for ten LCCO (light cracker cycle oil) storage tanks at a refinery can be found in TCEQ (2010). Uses for this gas oil intermediate stream include being used as cutter stock or (after treatment) being blended into diesel fuel. None of the tanks were heated, according to attachments C1 and C2 from that report, but nine of the ten tanks held liquid whose bulk temperature was elevated, presumably because the LCCO was hot when it was introduced to the tank. Reported bulk fluid temperatures range from 89°F to 150°F. All ten tanks had fixed roofs with no floating roof, with half having white shells and roofs and the other half having black shells and roofs (note that reported temperatures for the 5 black tanks averaged 112°F while temperatures for the four white tanks with elevated temperature averaged 98°F). The paint was in good condition for four of the five white tanks and one of the five black tanks. The paint for the remaining tanks was in poor condition. All of the black tanks were 117 ft in diameter and 42 ft high. Two of the white tanks were 150 ft in diameter and 39 ft high, two were 120 ft in diameter and 40 ft high, and one was 70 ft in diameter and 46 ft high.

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2. Heavy and light naphtha

Synonyms for heavy and light cracked naphtha from material safety data sheets for refinery #10 (Refinery #10 2006f, g) are as follows:

Light fluid gasoline: light catalytic cracked naphtha (petroleum), light naphtha from a fluid catalytic cracker unit (FCCU), FCCU light naphtha or gasoline, gasoline blending component, C4-C9 solvent or naphtha, C4-C9 petroleum hydrocarbons

Heavy fluid gasoline: FCCU heavy gasoline or naphtha, untreated cat cracked heavy gasoline, fluid unit gasoline splitter tower bottoms, FCCU C-006 tower bottoms, FCCU gasoline splitter reboiler feed and recycle streams, catalytic naphtha fractionator (CNF) feedstock, 735 unit CNF feed, magnaformer CNF feedstock, heavy catalytic cracked naphtha (petroleum), HCCN, C7-C12 petroleum hydrocarbons

Stream origins and destinations

One category of naphthas is the straight run naphthas that are a direct distillation cut between light gases and kerosene. They contain paraffins (saturated hydrocarbons), naphthenes (cyclic paraffins), and aromatics. There is no hard and fast rule that distinguishes between heavy and light naphtha, and some refineries also designate a medium naphtha stream that is treated differently from either the light naphtha or heavy naphtha streams.

The heavy naphtha stream from atmospheric distillation, which is generally comprised mostly of molecules with seven to 10 or 11 carbons, is usually sent to desulfurization and then reforming to boost the octane number before it is blended into gasoline.

The light naphtha from atmospheric distillation is also called paraffinic naphtha and light distillate feedstock. It usually has four, five, or six carbon atoms per molecule. Light naphthas are generally used as petrochemical feedstock. If they are sent to a steam cracker, light olefins are produced (ethylene, propylene, butadiene) in addition to light paraffins (ethane, propane, butane). When sent to reforming, benzene, xylene, and toluene are produced. This light naphtha stream may also be blended into gasoline or used to produce hydrogen.

Some naphtha streams are not straight run, most notably the naphtha from fluid catalytic cracking. There is also coker naphtha (see section on coker naphtha). These naphtha streams are usually treated and blended into gasoline.

Physical properties of streams

The vapor pressure at the average storage tank temperature (along with that temperature) are given for “Unfinished Oils – Naphthas and lighter” in 153 storage tanks in Texas in the supplementary Excel workbook titled “component 1 intermediate storage tanks Texas with corrected tank ids with STARS heat info sanitized.xlsx.”

Crude oil assays, which provide information about the expected products from distillation of various crudes, provide potentially useful information about the physical properties of distillation cuts like naphthas. The Energy Information Administration tracks information about crude imports by country

for each Petroleum Administration for Defense (PAD) District but finer detail about the specific domestic and imported crude charges at refineries does not seem to be available, other than anecdotally with no reference for the source of information. In any case, data on the properties of major distillation cuts for any crude oil adds to an understanding of the potential range of properties of naphthas.

Appendix A describes supplementary Excel workbooks that contain assay data from ExxonMobil for two crudes fed to refineries in Texas (ExxonMobil not dated a, b): HOOPS Blend (ExxonMobil not dated c) and Thunder Horse (ExxonMobil not dated d). These assays do not include some of the data that are useful for estimating storage tank emissions, like molecular weights or vapor pressures of the major distillation cuts.

An assay of Hibernia crude (Chevron 2011) is included in Appendix A because although this crude is not typically sold to Gulf Coast refineries, the assay provides an estimate for the molecular weight of the distillation cuts.

Another source of crude oil assays is Santos (not dated a, b, c, d, e). Santos is an energy services company operating in and around Australia and the crude oils it assayed are not expected to be utilized by Texas refineries. Their assays are included here because in some cases the Santos assays include vapor pressure and/or or molecular weights of the distillation cuts. The Santos assays and a more detailed description of the crude oils assayed are given in Appendix A.

The molecular weights of light catalytic naphtha at refinery #3, whose emissions were estimated for the Texas Commission on Environmental Quality, were 92 g/mol for vapor and 123 g/mol for liquid, and the Reid vapor pressure was 12.3 psi (TCEQ 2010).

The light fluid gasoline MSDS for refinery #10 (Refinery #10 2006f) gives the lowest known value for the boiling point of this stream as 69°C (156°F) and the weighted average boiling point as 83°C (181°F). The melting point range is not available. The specific gravity at 60°F is 0.7. The highest known vapor pressure is given as 16.5 kPa (124 mm Hg) at 20°C with a weighted average of 7.44 kPa (55.8 mm Hg) at 20°C. The viscosity is not available.

The heavy fluid gasoline MSDS for refinery #10 (Refinery #10 2006g) gives the boiling point range of this stream as 80-235°C (176-455°F) and the melting point is LT (less than) -46°C (-50°F). The specific gravity at 60°F is 0.83-0.85. The vapor pressure is given as 2.0-2.2 Reid-psi at 38°C (100 °F). The viscosity is 1-3 cSt at 40°C.

Composition of streams

The Thunder Horse and HOOPS blend assays described earlier (as well as the non-Texas fed assays) have a breakdown of hydrocarbon types (paraffins, naphthenes, aromatics) for the naphtha cuts. More information about these assays (along with other assays that contain this type of information for crude oils not fed to Texas refineries) is given in Appendix A of this report).

US EPA's SPECIATE 4.4 database (US EPA 2014a) contains a composite speciation of emissions from 9 tanks storing distillate oils from a study done in the early 1990s. While this study is ubiquitously

referenced and the data were being used to draft air permission permits as recently as 2013 (Minnesota Pollution Control Agency 2013), the original work was not found. It is possible that the tanks whose data were composited for SPECIATE were a combination of naphtha and gas oil tanks. The speciation data can be found in Appendix C. Nearly 30% of the emissions are attributed to n-butane and another nearly 30% are unidentified. It is important to remember that speciation in the vapor over a liquid mixture varies with temperature; temperatures were not provided in the SPECIATE data.

The MSDS for light fluid gasoline at refinery #10 (Refinery #10 2006f) says that this stream is 5-15% C6-C9 alpha alkenes, 5-15% hexane, other isomers, 1-10% n-hexane, 1-5% xylene, all isomers, 1-5% octanes, all isomers, 1-5% butenes or butylenes, 1-5% benzene, 1-5% cyclohexane, 1-5% toluene, 0.5-1.5% trimethylbenzenes, all isomers, 0.5-1.5% ethylmethylbenzene, all isomers, <1% 1,3-butadiene, 0.2-1% ethylbenzene, and <0.2% hydrogen sulfide. (Note that this list of constituents does not include all compounds in the stream.) The list of compounds found in the workplace exposure section of this MSDS may provide clues about the compounds present in the stream. This list is: hexane, other isomers; n-hexane; xylene, all isomers; octanes, all isomers; benzene; cyclohexane; toluene; trimethylbenzenes, all isomers; hydrogen sulfide; and 1,3-butadiene, and ethylbenzene.

The MSDS for heavy fluid gasoline at refinery #10 (Refinery #10 2006g) says that this stream is 0.1-0.5% benzene, 5-15% heptanes, 1-5% methylcyclohexane, 1-5% toluene, 5-15% C7-C12 alpha-alkenes, 15-25% octanes, 5-10% xylene, mixed isomers, 1-2% ethylbenzene, 10-25% nonanes, 0.5-1.5 n-propylbenzene, 5-10% trimethylbenzene (mixed isomers), 3-6% 1,2,4-trimethylbenzene (pseudocumene), 1-10% ethylmethylbenzenes (ethyltoluenes), 0.5-1.5% indene, 0.5-1.5% naphthalene, 5-10% C10-C12 alkylbenzenes, and 5-10% C10-C12 alkanes, isoparaffins, cycloalkanes, and naphthenes. (Note that this list of constituents does not necessarily include all compounds in the stream.) The list of compounds found in the workplace exposure section of this MSDS may provide clues about the compounds present in the stream. This list is: gasoline ("A3" animal carcinogen); petroleum distillates (naphtha); benzene ("A1" and "Z-2" carcinogen); heptane (n-heptane); methylcyclohexane; toluene ("A4"=not classifiable); octane, all isomers; xylene, mixed isomers ("A4"=not classifiable); ethylbenzene ("A4"=not classifiable); nonane, all isomers; trimethylbenzene (mixed isomers); indene; and naphthalene ("A4"=not classifiable). Under "volatile characteristics," this MSDS says "volatile organic compounds (VOCs) content=100%; 750-875 g/L."

Hansen (2014) gives the composition of "naphtha" in a storage tank at refinery #14 as follows:

Compound	Volume %
N-Pentane	18.3
N-Hexane	40.3
N-Heptane	22
1-Pentene	0.2
Cyclopentene	5.1
Benzene	4.4
Naphthalene	9.7

Capacity, stocks, and throughput

The US EPA’s refinery information collection request (US EPA not dated) asked for annual production of “Unfinished Oils – Naphthas and lighter.” These values are given in the “products produced” worksheet of the supplementary Excel workbook titled “component 1 Texas refinery details sanitized.xlsx.”

However, many of the quantity fields are blank, presumably because they were confidential business information.

Twenty-four refineries list “Unfinished Oils – Naphthas and lighter” as a product but only three provide an annual production value: refinery #xxx reports production in 2010 of 82,205 bbl, refinery #1 reports production in 2010 of 624,000 bbl, and refinery #13 reports production in 2010 of 692,000 bbl. Eleven of the 24 refineries in this group provided information about whether this stream was used onsite or transferred offsite. Five refineries (#7, #8, #19, #4b, and #12) report that all of the “Unfinished Oils – Naphthas and lighter” they produce are used onsite. Inexplicably, refinery #8 reports shipping modes (38% tank truck and 62% pipeline), even though they report 100% onsite usage. Four refineries (#6, #11, #15, and #xxx) report that none of the “Unfinished Oils – Naphthas and lighter” they produce are used onsite. The remaining two refineries (#1 and #13), report 14% and 18% onsite usage, respectively.

The US EPA’s refinery information collection request (US EPA not dated) also includes data on throughput by tank. The supplementary Excel workbook titled “component 1 intermediate storage tanks Texas with corrected tank ids with STARS heat info sanitized.xlsx” includes information about storage tanks at refineries in Texas holding “Unfinished Oils – Naphthas and lighter.” Many of the streams in the “other” category are also naphtha streams. A total of 166 tanks were reported to be holding intermediate naphthas (note that in a few cases some interpretation was required when determining which tanks held intermediate naphthas).

Reported throughput volumes vary widely amongst the stream categories. Average, maximum, and minimum throughputs for each of the naphtha stream categories are given in the table below.

Stream category	Throughput per tank in 2009, bbl				number of tanks in sample
	average	standard deviation	max	min	
Unfinished Oils – Naphthas and lighter	516,524	810,563	2,864,825	0	36
Sweet Naphtha	3,400	n/a	n/a	n/a	1
Sour Naphtha	416,868	592,143	1,100,584	69,340	3
Naphtha Reformer Feed	1,180,613	1,016,244	2,022,922	51,900	3
Heavy CAT Naphtha*	504,105	n/a	n/a	n/a	1
ISOM FEED*	90,676	128,235	181,352	0	2
Light Straight Run Gasoline	CBI				1
Unifier Feed	745,868	419,541	1,008,057	121,001	4

Note: CBI=confidential business information.

*These acronyms are not spelled out in the refinery information collection request data, but CAT probably stands for catalytic cracker and ISOM probably stands for isomerization unit.

Note that some tanks were reported to have a throughput of zero and that throughput is only available for 50 of the 166 tanks holding unfinished naphthas.

While individual refineries vary considerably in their configuration, the feed capacity for processes identified as naphtha upgrading might help to provide a sense of the potential volume of the production of intermediate naphthas.

Information about process capacities is contained in two of the supplementary Excel workbooks described in the section titled "Refineries in Texas." One source of capacity information is data collected from US EPA's refinery information collection request (US EPA not dated) and can be found in the "processes at refineries" worksheet in the "component 1 Texas refinery details sanitized.xlsx" workbook. Refineries in this workbook are identified by number.

Data from Koottungal (2013) were used to create another supplementary Excel workbook that gives charge capacities for many processes including hydrotreating by stream type and reforming charge capacities as of January 1, 2014. The refineries in this workbook are identified by number and by region (inland or Gulf Coast).

This table shows the values from both sets of data. This would not be expected to capture all of the intermediate naphtha capacity, as some naphtha streams might be upgraded without hydrotreating. However, those processes in aggregate are probably minor compared to what is captured here. These values do not overstate capacity (there is no double-counting).

refinery #	Capacity in barrels per calendar day			
	Koottungal 2013 (values as of Jan 1, 2014)			Desulfurization/ hydrotreating – naphtha/reformer feed, US EPA not dated (values for 2010)
	Naphtha hydrotreating other than pretreatment of catalytic reformer feeds	Catalytic reforming	Total naphtha hydrotreating other than pretreatment of catalytic reformer needs and catalytic reforming	
1	0	0	0	0
2	0	21,000	21,000	25,500
3	0	124,300	124,300	CBI (4 units)
4	0	45,450	45,450	0
5	11,200	33,800	45,000	55,700
6	0	17,500	17,500	22,000
7	113,500	120,000	233,500	CBI (3 units)
8	63,000	138,500	201,500	0
9	0	66,600	66,600	82,600
10	23,400	33,700	57,100	44,000
11	0	10,500	10,500	0
12	14,700	45,000	59,700	45,000
13	0	20,000	20,000	CBI (1 unit)
14	0	67,100	67,100	75,000
15	0	37,918	37,918	55,000
16	0	47,000	47,000	57,650
17	9,500	0	9,500	0
18	30,000	53,000	83,000	0
19	22,000	47,400	69,400	63,500
20	0	14,500	14,500	0
21	0	34,000	34,000	25,000
22	0	18,000	18,000	30,100 ²
23	0	29,000	29,000	134,000
xxx	No data	No data	No data	0
Total all	287,300	1,024,268	1,311,568	¹

Notes: CBI=confidential business information

¹No total is given here because it would be distorted by the missing information from refineries with confidential business information claims.

²There was no capacity information for one of the 5 hydrotreaters for this refinery (one of five units was blank, presumably due to CBI).

The two sets of data are in fairly reasonable agreement except for refinery #23.

Data about the month-to-month change in stored quantities of intermediate heavy and light naphthas may shed light on tank turnover rates as well. The US Energy Information Administration (US EIA) tracks information about refinery stocks of unfinished oils categorized as “naphthas and lighter.” US EIA data for Texas is divided into Gulf Coast and inland refineries (individual refinery data is not published). The following table shows the most recent 12 months of data. US EIA defines “unfinished oils” as all oils requiring further processing, except those requiring only mechanical blending.” They do not provide an explanation of what is included in “naphthas and lighter,” but they define “naphtha” as a petroleum fraction with an approximate boiling range of 122-400° F (US EIA not dated).

From US EIA (2014k):

Date	Refining District Texas Inland Naphthas and Lighter Stocks at Refineries (Thousand Barrels)	Refining District Texas Gulf Coast Naphthas and Lighter Stocks at Refineries (Thousand Barrels)
May-2013	2,023	5,099
Jun-2013	1,879	5,117
Jul-2013	1,810	4,995
Aug-2013	1,583	5,003
Sep-2013	1,449	5,473
Oct-2013	1,554	5,337
Nov-2013	1,465	5,485
Dec-2013	1,378	5,096
Jan-2014	1,564	4,907
Feb-2014	1,564	5,387
Mar-2014	1,766	5,160
Apr-2014	2,219	5,329

Storage tank characteristics

Detailed information about storage tanks holding intermediates was obtained during the US EPA’s refinery information collection request (US EPA not dated). The supplementary Excel workbook titled “component 1 intermediate storage tanks Texas with corrected tank ids with STARS heat info sanitized.xlsx” includes information about storage tanks at refineries in Texas holding “Unfinished Oils – Naphthas and lighter.” This includes type of tank, dimensions, average storage temperature, types of rim seals, how many times the roof was landed (for floating roof tanks) and what type of controls were used the last time the tank was degassed. This information may reveal whether the same tank was used for more than one product.

A total of 166 tanks were reported to be holding intermediate naphthas (note that in a few cases some interpretation was required when determining which tanks held gas oils). Tank types for each stream category are given in the following table.

Stream category	Number of tanks					
	Fixed roof tank vented to atmosphere	External floating roof	Internal floating roof	Pressurized/sphere tank	Cone roof tank	Total
Unfinished Oils – Naphthas and lighter	9	71	48	23	0	
Sweet Naphtha		1				
Sour Naphtha		2	1			
Naphtha Reformer Feed		3				
Heavy CAT* Naphtha		1				
Light straight run gasoline				1		
ISOM* FEED					2	
Unifier Feed		1	3			
Total	9	79	52	24	2	166

*These acronyms are not spelled out in the refinery information collection request data, but CAT probably stands for catalytic cracker and ISOM probably stands for isomerization unit.

Tank sizes vary widely amongst the different stream categories. Average, maximum, and minimum tank sizes for each of the stream categories are given in the table below.

Stream category	Number of tanks in sample	Tank capacity, ft ³			
		average	standard deviation	max	min
Unfinished Oils – Naphthas and lighter	134	357,333	260,687	1,270,032	4,451
Sweet Naphtha	0	Maximum liquid height not given for any tanks			
Sour Naphtha	0	Maximum liquid height not given for any tanks			
Naphtha Reformer Feed	3	372,997	162,568	512,107	194,288
Heavy CAT* Naphtha	1	412,596	n/a	412,596	412,596
ISOM* FEED	0	Maximum liquid height not given for any tanks			
Light Straight Run Gasoline	1	298,055	n/a	298,055	298,055
Unifier Feed	4	174,872	187,803	446,508	13,956

*These acronyms are not spelled out in the refinery information collection request data, but CAT probably stands for catalytic cracker and ISOM probably stands for isomerization unit.

Tank capacity and throughput are not closely related. The average throughput:capacity ratio for these streams is 3.1 bbl/ft³ with a standard deviation of 2.7 bbl/ft³ (it was possible to calculate this ratio for 34 tanks).

Reported temperatures amongst the stream categories are more uniform than capacity. Average, maximum, and minimum temperatures for each of the stream categories are given in the table below.

Stream category	Temperature, °F				number of tanks in sample
	average	standard deviation	max	min	
Unfinished Oils – Naphthas and lighter	83	15	119	-25	144
Sweet Naphtha	95	n/a	n/a	n/a	1
Sour Naphtha	87	14	95	70	3
Naphtha Reformer Feed	92	0	92	92	3
Heavy CAT* Naphtha	92	n/a	n/a	n/a	1
ISOM* FEED	70	0	70	70	2
Light Straight Run Gasoline	77	n/a	n/a	n/a	1
Unifier Feed	93	4	99	90	4

*These acronyms are not spelled out in the refinery information collection request data, but CAT probably stands for catalytic cracker and ISOM probably stands for isomerization unit.

Detailed information used to develop emission estimates for three light cat naphtha storage tanks at a refinery can be found in TCEQ (2010). This intermediate stream would be blended into gasoline (generally after treating unless treating was done before storage). None of the tanks were heated but one held liquid whose bulk temperature was slightly elevated (to 90.2°F), presumably because the naphtha was hot when it was introduced to the tank. All three tanks had steel pontoon external floating roofs (no fixed roof). All three tank roofs and shells were painted white, with one in poor condition and the other two in good condition. One of the tanks was 150 ft in diameter and 48 ft high, and the other two were 117 ft in diameter and 42 ft high. All three tanks had mechanical-shoe primary rim seals, one gauge hatch with a gasketed cover, and two vacuum breakers with a gasketed cover. The smaller tanks had a rim mounted secondary rim seal, an unslotted guide pole with a gasket, pole wiper, and no float or sleeve, a gasketed and bolted hatch, 8 pontoon-area legs, 17 center-area legs, and 2 rim vents with gasketed covers. The larger tank had a shoe mounted secondary rim seal, a slotted guide pole with a gasket, pole wiper, and a pole sleeve, two gasketed and bolted hatches, 24 pontoon-area legs, 36 center-area legs, and 2 rim vents with ungasketed covers.

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3. Atmospheric and vacuum tower bottoms

Atmospheric and vacuum tower bottoms are types of refinery residuum. Other types of residuum are covered in the section titled “Residuum.”

Stream origins and destinations

The American Petroleum Institute defines atmospheric tower residues as a “complex residuum from the atmospheric distillation of crude oil. It consists of hydrocarbons having carbon numbers predominantly greater than C20 and boiling above approximately 350 °C (662°F)” (US EPA 2004). They are usually sent to a vacuum distillation tower (if present). The bottoms from vacuum distillation can be sent to a coker to create lighter, higher value products with coke as a byproduct. If the crude charge is a heavy crude, the vacuum bottoms may consist of straight-run asphalt. The vacuum bottoms might also be sent to deasphalting or asphalt blowing. Atmospheric bottoms or vacuum bottoms can be sent to visbreaking, for example, to make them less viscous, which is desirable because, for example, lower viscosity streams require less cutter stock when blending to create heavy fuel oil product. In some cases, the product of visbreaking is distilled to separate material that can be made into fuels from a hard residue that can be blended into asphalt products (Asphalt Institute Inc. and European Bitumen Association – Eurobitume 2011). No visbreaking is reported at refineries in Texas (Koottungal 2013).

At the present time, most heavy fuel oils (residual fuels) consist primarily of vacuum tower residues and residues from thermal and catalytic cracking (US EPA 2004). In fact, the American Petroleum Institute’s definition of heavy fuel oil is, in part “the liquid product from various refinery streams, usually residues” (US EPA 2004). To lower the viscosity into a desirable heavy fuel oil range (such as No. 6 fuel oil), the residual streams are mixed with cutter stock. This cutter stock could be any one of a number of low value distillate streams and would vary from refinery to refinery as well as from time to time within the same refinery.

It is difficult to generalize about the destination of tower bottoms because their basic nature varies widely from refinery to refinery and crude to crude. For example, the crude oil assays from Santos (not dated a, b, c, d, e) resulted in an expected pour point for the Cooper Basin crude oil vacuum bottoms of 39°C, which is the same as the expected pour point for the vacuum gas oil of the Mutineer-Exeter crude. Also, the atmospheric bottoms from Barrow Island and Stag crude are expected to be liquid at room temperature. Lighter tower bottoms might be blended directly into fuel oil while heavier ones would undergo further processing before blending into fuel oil.

Physical properties of streams

The vapor pressure at the average storage tank temperature (along with that temperature) are given for “Unfinished Oils – Residuum” in 25 storage tanks in Texas in the supplementary Excel workbook titled “component 1 intermediate storage tanks Texas with corrected tank ids with STARS heat info sanitized.xlsx.” These tanks could hold atmospheric and tower bottoms or other residue. There are also some storage tanks whose contents were described as “other” that could contain atmospheric and vacuum tower bottoms.

Crude oil assays, which provide information about the expected products from distillation of various crudes, provide potentially useful information about the physical properties of distillation cuts like atmospheric and vacuum tower bottoms. The Energy Information Administration tracks information about crude imports by country for each Petroleum Administration for Defense (PAD) District but finer detail about the specific domestic and imported crude charges at refineries does not seem to be available, other than anecdotally with no reference for the source of information. In any case, data on the properties of major distillation cuts for any crude oil adds to an understanding of the potential range of properties of atmospheric and vacuum tower bottoms.

Appendix A describes supplementary Excel workbooks that contain assay data from ExxonMobil for two crudes fed to refineries in Texas (ExxonMobil not dated a, b): HOOPS Blend (ExxonMobil not dated c) and Thunder Horse (ExxonMobil not dated d). These assays do not include some of the data that are useful for estimating storage tank emissions, like molecular weights or vapor pressures of the major distillation cuts.

An assay of Hibernia crude (Chevron 2011) is included in Appendix A because although this crude is not typically sold to Gulf Coast refineries, the assay provides an estimate for the molecular weight of the distillation cuts.

Another source of crude oil assays is Santos (not dated a, b, c, d, e). Santos is an energy services company operating in and around Australia and the crude oils it assayed are not expected to be utilized by Texas refineries. Their assays are included here because in some cases the Santos assays include vapor pressure and/or or molecular weights of the distillation cuts. The Santos assays and a more detailed description of the crude oils assayed are given in Appendix A of this report.

US EPA (2012) reported a pour point value for atmospheric tower bottoms residue of 18°C.

Stratiev and others (2008) give viscosity at various temperatures for virgin vacuum tower residue:

Temperature, °C.	Viscosity, Pa-sec
Virgin vacuum residue 1	
80	6.333
90	2.727
100	1.303
110	0.727
120	0.424
Virgin vacuum residue 2	
80	1.697
90	0.879
100	0.485
110	0.272
120	0.152

Measured values (using ASTM D2879) of the vapor pressure of vacuum residual oil in psia (before cutting) are given here (API 2012 with 2013 addendum):

Temperature, °F	Sample ID			
	A3	B3	C3	D3
32	.00015	.00012	.00000	.00002
68	.00052	.00039	.00002	.00009
100	.00128	.00101	.00005	.0028
150	.00464	.00367	.00029	.00131
200	.01315	.01044	.00101	.00464
250	.03287	.02514	.00387	.01354
300	.07348	.05801	.01160	.03674
350	.14696	.11989	.02901	.07735
400	.27071	.22237	.06575	.18177
450	.46408	.37707	.13149	.33839
500	.73480	.61878	.25138	.59944
550*	1.2	1.0	0.5	1.1
600*	1.7	1.5	0.8	1.7
650*	2.5	2.1	1.3	2.6
700*	3.5	3.0	2.0	4.1

*Reported in Torr in source and converted to psi.

The API gravities of the four samples were 5.7, 9.8, 16.4, and 5.3 for A3, B3, C3, and D3, respectively (API 2012 with 2013 addendum). The vapor pressures in this table were measured using an isoteniscope. The vapor pressures of these streams measured using the Heavy Oil Storage Tank Committee (HOST) method at 340°F are 0.023 and 0.021 psia for stream A3 and B3, respectively (no data for stream C3 and D3).

API (2012c with 2013 addendum, Table 2) provides default properties for vacuum residual oil. Like many intermediate streams, the properties of this stream tend to vary widely from refinery to refinery.

Composition of streams

According to US EPA (2004), a representative sample of atmospheric tower residue was 68% aromatics. The American Petroleum Institute’s definition of atmospheric tower residue says that this stream is likely to contain 5 wt % or more of 4- to 6-membered condensed ring aromatic hydrocarbons (US EPA 2004).

Capacity, stocks, and throughput

The US EPA’s refinery information collection request (US EPA not dated) asked for annual production of “Unfinished Oils – residuum.” These values are given in the “products produced” worksheet of the supplementary Excel workbook titled “component 1 Texas refinery details sanitized.xlsx.” However, many of the quantity fields are blank, presumably because they were confidential business information. Also, data identified as “Unfinished Oils – residuum” is expected to include contain residuum other than distillation tower bottoms.

Sixteen refineries list “Unfinished Oils – Residuum” as a product but only one provides an annual production value: refinery #13 reports production in 2010 of 275,000 bbl. Seven of the 16 refineries in this group provided information about whether this stream was used onsite or transferred offsite. Two refineries (#6 and #7) reported that none of the “Unfinished Oils – Residuum” they produce are used onsite, while another two refineries (#4b and #13) report that 100% of this stream is used onsite. One refinery (#11) reported zeroes for all onsite and offsite usage and another refinery (#8) reported 20% shipped by barge with zeroes for other onsite and offsite usage. The remaining refinery (#19) reported 80% onsite usage.

The US EPA’s refinery information collection request (US EPA not dated) also includes data on throughput by tank. The supplementary Excel workbook titled “component 1 intermediate storage tanks Texas with corrected tank ids with STARS heat info sanitized.xlsx” includes information about storage tanks at refineries in Texas holding “Unfinished Oils – Residuum.” Many of the streams in the “other” category are also residual streams. A total of 37 tanks were reported to be holding residuum (note that in a few cases some interpretation was required when determining which tanks held residuum). Five of these tanks held carbon black oil, three tanks held vacuum tower bottoms, and the remaining 29 tanks held streams that were not described in enough detail to know whether they held tower bottoms or some other residual. All but the carbon black oil tanks are included in the analysis in this section.

Reported throughput volumes vary widely amongst the stream categories. Average, maximum, and minimum throughputs for each of the gas oil stream categories are given in the table below.

Stream category	Throughput per tank in 2009, bbl				number of tanks in sample
	average	standard deviation	max	min	
Unfinished Oils – Residuum	1,183,222	1,960,650	5,884,476	0	11
Coker feed (unspecified, heavy, and light)	1,722,290	1,817,593	3,463,546	12,736	4
VTB*	977,030	1,692,050	2,930,841	0	3

*This acronym is not spelled out in the refinery information collection request data, but VTB probably stands for vacuum tower bottoms.

Note that some tanks were reported to have a throughput of 0 and that throughput is only available for 18 of the 32 tanks holding unspecified residuum and vacuum tower bottoms.

The feed capacity for vacuum distillation provides a sense of the potential volume of the production of atmospheric tower bottoms.

Information about process capacities is contained in two of the supplementary Excel workbooks described in the section titled "Refineries in Texas." One source of capacity information is data collected from US EPA's refinery information collection request (US EPA not dated) and can be found in the "processes at refineries" worksheet in the "component 1 Texas refinery details sanitized.xlsx" workbook. Refineries in this workbook are identified by number.

Data from Koottungal (2013) were used to create another supplementary Excel workbook that gives charge capacities for many processes including vacuum distillation as of January 1, 2014. The refineries in this workbook are identified by number and by region (inland or Gulf Coast).

This table shows the values for vacuum distillation capacity from both sets of data.

refinery #	Vacuum distillation, capacity in barrels per calendar day	
	Koottungal 2013 (values as of Jan 1, 2014)	US EPA not dated (values for 2010)
1	0	0
2	24,000	24,000
3	225,150	0
4	73,625	77,000
5	125,500	132,066
6	15,000	CBI
7	285,000	CBI
8	143,000	0
9	83,125	87,500
10	191,100	202,000
11	0	0
12	138,000	138,000
13	41,000	0
14	173,100	180,000
15	106,247	109,000
16	95,000	90,000
17	39,000	40,000 ¹
18	145,000	220,000
19	53,200	51,000
20	130,000	41,000
21	35,000	36,000
22	34,700	51,600
23	75,000	80,000
xxx	No data	25,000
Total all	2,230,747	²

Notes: CBI=confidential business information

¹The capacity of a unit coded as a vacuum distillation tower but described as “Fuel Gas Amine Absorber – ULSD” was excluded from this analysis.

²No totals are given here because they would be distorted by the missing information from refineries with confidential business information claims.

Some of the refineries that reported other processes in US EPA (not dated) and that are reported by Koottungal (2013) to have vacuum distillation capacity did not report any vacuum distillation in US EPA (not dated) (refineries #3, #8, and #13). This is distinguished from refineries who reported vacuum distillation but have a blank capacity field, which is presumably due to confidential business information.

Data about the month-to-month change in stored quantities of residuum may shed light on tank turnover rates. The US Energy Information Administration (US EIA) tracks information about refinery stocks of unfinished oils characterized as residuum. US EIA data for Texas is divided into Gulf Coast and inland refineries (individual refinery data is not published). The following table shows the most recent 12 months of data. US EIA defines “unfinished oils” as all oils requiring further processing, except those

requiring only mechanical blending. Residuum is described as residue from crude oil after distilling off all but the heaviest components, with a boiling range greater than 1000°F (US EIA not dated).

From US EIA (2014l):

Date	Refining District Texas Inland Residuum Stocks at Refineries (Thousand Barrels)	Refining District Texas Gulf Coast Residuum Stocks at Refineries (Thousand Barrels)
May-2013	543	3,071
Jun-2013	643	2,694
Jul-2013	663	2,864
Aug-2013	648	3,647
Sep-2013	688	2,928
Oct-2013	877	2,898
Nov-2013	624	2,339
Dec-2013	558	2,701
Jan-2014	505	2,396
Feb-2014	485	2,448
Mar-2014	498	2,669
Apr-2014	730	2,344

Note that this table would contain stocks other than atmospheric and vacuum distillation bottoms and is repeated in the later section on residuum.

Storage tank characteristics

Detailed information about storage tanks holding intermediates was obtained during the US EPA’s refinery information collection request (US EPA not dated). The supplementary Excel workbook titled “component 1 intermediate storage tanks Texas with corrected tank ids with STARS heat info sanitized.xlsx” includes information about storage tanks at refineries in Texas holding “Unfinished Oils – Residuum” (no distinction is made between sources of residuum in this set of data). This includes type of tank, dimensions, average storage temperature, types of rim seals, how many times the roof was landed (for floating roof tanks) and what type of controls were used the last time the tank was degassed. This information may reveal whether the same tank was used for more than one product. There is no information about insulation or type of heater used for heated tanks. Many of the streams in the “other” category are also residual streams that could perhaps be atmospheric and vacuum tower bottoms.

A total of 32 tanks were reported to be holding residuum/vacuum tower bottoms (note that some interpretation was required when determining which tanks hold residuum/vacuum tower bottoms). All of the reported residuum/vacuum tower bottoms storage tanks in Texas fixed roof tanks vented to the atmosphere except for one tank holding “heavy coker” and the three tanks holding “VTB,” (presumably vacuum tower bottoms) which were cone roof tanks.

Average, maximum, and minimum tank sizes for each of the stream categories are given in the table below.

Stream category	Number of tanks in sample	Tank capacity, ft ³			
		average	standard deviation	max	min
Unfinished Oils – Residuum	25	404,976	384,795	1,372,180	107,388
Coker feed (unspecified, heavy, and light)	3	186,879	139,423	267,375	25,887
VTB*	0	No data			

*This acronym is not spelled out in the refinery information collection request data, but VTB probably stands for vacuum tower bottoms.

For the 14 vacuum tower bottoms/residuum storage tanks with both capacity and throughput data, the average throughput:capacity ratio was 6 bbl of throughput/ft³ of capacity (standard deviation of 9 bbl of throughput/ft³ of capacity).

Average, maximum, and minimum temperatures for each of the stream categories are given in the table below.

Stream category	Temperature, °F				number of tanks in sample
	average	standard deviation	max	min	
Unfinished Oils – Residuum	113	66	362	75	24
Coker feed (unspecified, heavy, and light)	232	116	320	70	4
VTB*	70	0	70	70	3

*This acronym is not spelled out in the refinery information collection request data, but VTB probably stands for vacuum tower bottoms.

As with asphalts and other residuum, the minimum pumping temperature of atmospheric and vacuum tower bottoms would generally be the temperature at which the viscosity is 2 Pa-s (Błażejowski et al 2014). Given this guideline, if the viscosity of the material in the tank is known at any temperature, the temperature that results in a viscosity of 2 Pa-s, which can be calculated using the correlation for predicting viscosities of asphalts and heavy oils at various temperatures, would provide a general idea of the minimum temperature of a tank holding atmospheric or vacuum tower bottoms, unless storage was expected to be long term. A more complete explanation of the calculations involved is given in the section on methods for estimating emissions from storage tanks.

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4. Asphalt

Deygout (2010) found that emissions of volatile organic compounds from tanks holding asphalt at a fully integrated refinery complex contributed about 5% of the overall volatile organic compound emissions from the refinery.

Stream origins and destinations

Asphalt occurs naturally and can be produced during refining of crude oils that contain asphaltenes. Outside of the US, it is often called bitumen. Depending on the crude and the distillation configuration, asphalt can be a straight run product of distillation (e.g., vacuum bottoms) or it can be further processed, or blended with processed residuum. Oxidation processes that increase the softening point are a major process by which asphalt is produced. Another major process is solvent deasphalting of vacuum residue. A material that can be blended into asphalt can also be produced by distillation of visbreaker output (Asphalt Institute Inc. and European Bitumen Association – Eurobitume 2011). Solvent extraction of vacuum residue and of feed streams to catalytic crackers, hydrocracking, and hydrodesulfurization (Houde and McGrath 2006) are minor contributors to worldwide asphalt production (Asphalt Institute Inc. and European Bitumen Association – Eurobitume 2011), but may be important to an individual refinery.

Most asphalt is used to build roads; the major types of asphalt produced are road oil, cutback asphalt, asphalt emulsion, and solid asphalt (Speight 2014).

Oxidation, or blowing is used to harden soft asphalt. In this process, air is blown at through the soft asphalt at approximately 500°F (Speight 2014).

When solvent deasphalting is applied to vacuum residue, it separates asphaltenes from residues that can be used in the production of lube oil. Typical deasphalting processes use propane, butane, isobutene, pentane, or supercritical solvent extraction (the residuum oil supercritical extraction or ROSE process) (Asphalt Institute Inc. and European Bitumen Association – Eurobitume 2011).

Asphalt is typically heated to 284°F so that it will liquefy and be easier to transport (Asphalt Institute Inc. and European Bitumen Association – Eurobitume 2011).

Sometimes, for ease of handling, liquid asphalt is created by mixing asphalt with a solvent (cutter stock) such as naphtha, kerosene, or gas oil at 225°F (cutback asphalt) (Speight 2014). Stoddard solvent is also used as cutter stock for cutback asphalt (Asphalt Institute Inc. and European Bitumen Association – Eurobitume 2011). US EPA (2004) says that refinery cutter stock with low polyaromatic hydrocarbon levels is sometimes used in cutback asphalt, which suggests that the cutter stock used in cutback asphalt has fewer problematic compounds than the cutter stock used in heavy fuel oils. After application, the solvent evaporates, leaving behind the asphalt. Rapid-curing asphalt is cut with 40-50% cutter stock in the naphtha or gasoline range, medium-curing asphalt is cut with cutter stock in the kerosene range, and slow-curing asphalt is cut with 25% cutter stock in the gas oil range (Speight 2014). Slow-curing asphalt is also called road asphalt or road oil (Speight 2014).

Liquid asphalt can also be made by grinding asphalt to a 5-10 μm size range and emulsifying with water in the presence of heat and an emulsifier such as colloidal clay or soap (emulsified asphalt) (Speight 2014).

Sometimes polymers, crumb rubber, sulfur, or polyphosphoric acid is added to asphalt to modify its properties. Asphalt blending/emulsifying/cutting may occur at the refinery or by a 3rd party outside the refinery (Asphalt Institute Inc. and European Bitumen Association – Eurobitume 2011).

Sometimes asphalt is sent to delayed coking or fuel oil blending (US EPA 1996).

Physical properties of streams

The vapor pressure at the average storage tank temperature (along with that temperature) are given for “Asphalt and Road Oil” in 18 storage tanks in Texas in the supplementary Excel workbook titled “component 1 intermediate storage tanks Texas with corrected tank ids with STARS heat info sanitized.xlsx.” There are also some storage tanks whose contents were described as “other” that contain asphalt.

Trumbore (1999) contains information about vapor pressure as a function of temperature and vapor and liquid molecular weights for three forms of asphalt: flux, paving, and oxidized (flux asphalt in this case probably refers to cutback asphalt). Oxidized asphalt is described as vacuum tower bottoms that have been fed to a blowing process, and paving asphalt is described as vacuum tower bottoms that meet paving specifications. Thus, these would be refinery product streams, not intermediates; it may be that the paving asphalts undergo processing to form slurries but that is not discussed in the article. Flux asphalts, on the other hand, are described as vacuum tower bottoms that can be fed to a blowing process to make oxidized asphalts. The flux asphalts from this study are probably most representative of intermediate asphalt streams at a refinery.

The data in Trumbore (1999) were developed from an Owens Corning study that included experimental values from 31 asphalt samples and was conducted in order to aid Owens Corning in its preparation of emission estimates from its asphalt storage tanks for Title V permit applications. Average values were calculated for each category of asphalt. As Trumbore (1999) notes, “[a]sphalts from different crude oil sources and from different processes will differ in composition and vapor pressure.” Indeed, Trumbore (1999) presents a comparison of correlated and measured values for oxidized asphalts and some of the individual samples differ from the average result by nearly an order of magnitude. It would not be unreasonable to assume that of the three types of asphalt, oxidized asphalt is likely to be the most uniform from one sample to the next and there is even more variation amongst flux asphalts. However, the values presented in Trumbore provide a relatively rich source of information.

From Trumbore (1999):

Table 2. Vapor Pressure Correlations for Asphalts

For the Clausius Clapeyron Equation
 $\ln V_p (\text{mm Hg}^1) = a - b/T(\text{R}^2)$

Class of Asphalt	a	b	n	Average correlation coefficient
Flux	18.2891	12725.60	10	-0.99976
Paving	20.7962	15032.54	8	-0.99985
Oxidized	18.8642	13458.56	13	-0.99991

For a log log Equation
 $\log V_p (\text{mm Hg}) = A * \log T (\text{F}^3) + B$

Class of Asphalt	a	b	n	Average correlation coefficient
Flux	7.0850	-16.8999	10	0.99736
Paving	7.8871	-19.0600	8	0.99965
Oxidized	7.0607	-16.9570	13	0.99981

1. 1 Pa = 0.0075 mm Hg
2. 1 K = (R - 492) * 5/9 + 273
3. 1 C = (F - 32) * 5/9

This journal article was digitized in such a way that many typos resulted. For clarity, the units of temperature in the Clausius-Clapeyron equation are Rankine. The units of temperature for the log log equation are in Fahrenheit and the row below the “paving” row in the log log equation should be labeled “oxidized.”

By studying both tanks in the field and conducting laboratory experiments, Deygout (2010) found that storage temperature (and by extension, vapor pressure) was not an important factor in predicting standing losses of volatile organics (C4 to C14) from asphalt storage tanks (for storage temperatures between 130 and 190°C). Instead, emissions were influenced by

1. The freshness of the asphalt being stored, with higher emissions coming from fresh asphalt. For the straight-run asphalt, emissions decreased by two-thirds when measured 18.5 hours after production as opposed to 1 hr.
2. The extent of stirring in the tank, with a greater intensity of mixing associated with higher emissions.
3. The type of asphalt being stored. During the blowing process, blown (aka oxidized) asphalt is stripped of volatile organic compounds and the emissions from tanks storing blown asphalt were found to be roughly one-fourth the emissions from tanks storing straight-run asphalt and visbreaker-cracked residue.

This figure shows the decline in emissions over time (Deygout 2010). Note that the x-axis scale is not linear and the decay in emissions between t=1 hr and t=18.5 hrs is steep:

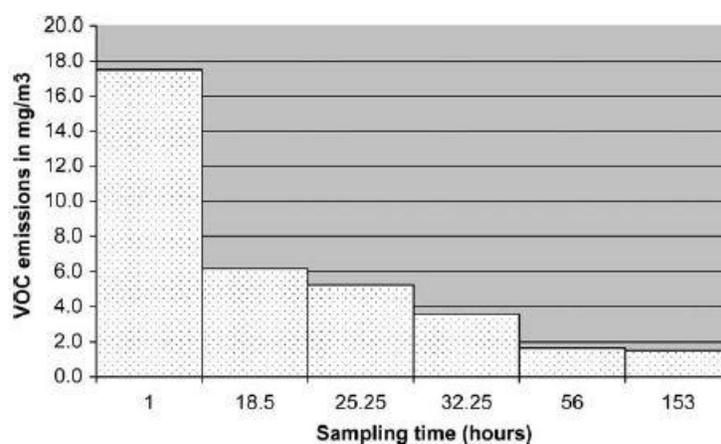


Figure 4. Quantitative depletion over time (S_R at 180°C).

In this figure, S_R refers to straight-run asphalt.

This table shows standing emissions as measured from storage tanks in the field holding three different types of asphalt (Deygout 2010):

Table 3. Calculated NMVOC concentrations and emissions.

Binder type	Dry VOCs (ppm)	Wet VOCs (mg/m ³)	Emitted VOCs (g/h)	Emitted VOCs (kg/yr)
OB	279	1428	42.8	375
CR	1103	5630	168.9	1480
SR	1133	5792	173.8	1522

In this table, OB is oxidized asphalt, CR is visbreaker-cracked residue, and SR is straight-run asphalt. The measurements that the Table 3 values were based on were taken on tanks holding “fresh” asphalt, i.e. asphalt that had been held only a few days. As Deygout’s (2010) Figure 4 shows, however, emissions are much higher in the first hour of holding than they are a few days later.

Deygout (2010) found that the average molecular weight of the volatile organic compounds in the tank emissions was very similar for all three types of asphalt, at 125-126 g/mol.

From Asphalt Institute Inc. and European Bitumen Association – Eurobitume 2011:

Table 1 - Typical physical properties for bitumen

Property	Test Method	Value
Flash Point, °C, Cleveland Open Cup	ASTM D92, EN 22592 (b)	Varies according to grade; Typically >230°C (445°F)*. >270°C (520°F) in ASTM D312, >250°C (482°F) in EN 13304
Loss on Heating, %m (Maximum)	ASTM D2872, EN 12607-1	0.5-1% maximum depending upon the specification
Specific gravity value	ASTM D70 EN 15326	≥0.95, typically >1.0, not a specification
Solubility, % (Minimum)	ASTM D2042, EN 12592	≥99% _m by specification (Trichloroethylene, Toluene, or Xylene as specified)
Solubility in water		Negligible
Softening Point	ASTM D36, EN 1427	>30°C (86°F), grade dependent
Vapour Pressure		Below detection limit at ambient temperature

* Flash point varies with bitumen type. In some regions softer bitumens may have a significantly lower value

Composition of streams

The lowest molecular weights of the compounds in asphalt depend on the cut point of the distillation process and start at around 300 g/mol. There are few, if any, molecules with a molecular weight higher than 1000 g/mol (Asphalt Institute Inc. and European Bitumen Association – Eurobitume 2011).

The composition of asphalts varies widely. The following figure pictures the classes of compounds found in asphalt; below it, their characteristics are summarized (Asphalt Institute Inc. and European Bitumen Association – Eurobitume 2011):

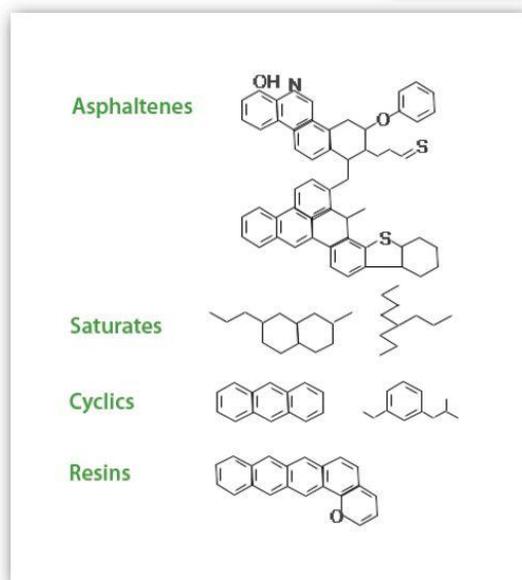


Figure 7 -Example of the broad chemical types present in bitumen

- By mass, cyclics usually make up the largest class of compounds in asphalt (ranging from 30-60%). These compounds have aromatic or naphthenic nuclei and side chain constituents and their molecular weights range from a number average of 500-900. They are viscous liquids at room temperature.
- Resins are generally the next largest class of compounds in asphalt, making up 15-55% by mass. They are polar aromatics and are solid or semi-solid. Their molecular weights range from 800-2000 (number average).
- Asphaltenes, which are solid, highly polar aromatics of high molecular weight that contain some nitrogen, oxygen, and sulfur in addition to nickel and vanadium, make up 5-31% of asphalt by mass.
- Saturates made up of straight and branched hydrocarbons plus some alkyl naphthenes and alkyl aromatics make up another 5-20% by mass. Saturates have a molecular weight similar to cyclics and can be waxy or non-waxy.

Oxygenation to create blown asphalt converts cyclics to resins to asphaltenes (Asphalt Institute Inc. and European Bitumen Association – Eurobitume 2011).

From Asphalt Institute Inc. and European Bitumen Association – Eurobitume 2011 (referencing 1986 data):

Table 2 - Elemental analysis of bitumens from various sources²⁴

Element	Range	Average
Carbon, %w	80.2 - 84.3	82.8
Hydrogen, %w	9.8 - 10.8	10.2
Nitrogen, %w	0.2 - 1.2	0.7
Sulphur, %w	0.9 - 6.6	3.8
Oxygen, %w	0.4 - 1.0	0.7
Nickel, ppm	10 - 139	83
Vanadium, ppm	7 - 1590	254
Iron, ppm	5 - 147	67
Manganese, ppm	0.1 - 3.7	1.1
Calcium, ppm	1 - 335	118
Magnesium, ppm	1 - 134	26
Sodium, ppm	6 - 159	63

Deygout (2010) found that in the laboratory, the feed to asphalt oxidizers has three times the volatile organic carbon emissions as the oxidized asphalt.

Asphalt production does not create PAHs but some of the PAHs found in crude oil make their way to asphalt. From Asphalt Institute Inc. and European Bitumen Association – Eurobitume 2011:

PAH	PAH in Bitumen ^{32,33,34}	PAH in bitumen fumes (personal samples ^{*)} ³⁵	
	mg/kg (ppmw)	µg/m ³	Standard deviation
Naphthalene	2.5 - 3.0	5.5 (8/9)**	2.9
Acenaphthene	BDL - 0.7	3.3 (1/9)	7.8
Acenaphthylene	NR	3.3 (2/9)	8.5
Fluorene	0.3 - 0.5	0.47 (1/9)	0.84
Phenanthrene	0.3 - 7.3	0.82 (2/9)	2.2
Anthracene	BDL - 2.0	0.063 (1/9)	0.074
Fluoranthene	BDL - 2.0	0.98 (1/9)	2.6
Pyrene	0.2 - 8.3	NA	
Chrysene	<0.1 - 11	NA	
Benzo(a)anthracene	BDL - 3.3	NR	
Perylene	BDL - 39	NR	
Benzofluoranthenes	BDL - 1.2	0.65 (1/9)	1.7
Benzo(e)pyrene	<0.1 - 13	0.78 (1/9)	1.7
Benzo(a)pyrene	BDL - 4.6	0.16 (1/44)	0.072
Dibenzanthracenes	BDL - 3.3	NR	
Indeno(1,2,3-cd)pyrene	BDL - 2.4	NR	
Benzo(ghi)perylene	<0.1 - 4.6	NR	
Anthanthrene	BDL - 0.1	NR	
Dibenzo(al)pyrene	BDL - <0.6	NR	
Dibenzo(ai)pyrene	BDL - <0.6	NR	
Coronene	BDL - 1.9	NR	

* Personal exposure monitoring at terminals and refineries
 ** Results represent arithmetic mean of samples; (numbers in parentheses indicate numbers of samples above the limit of detection/number of samples)
 NA = Not Applicable
 NR = Not Reported
 BDL = Below Detection Limit
 Note: data on PAH content of bitumen and those for PAH in fumes are from different studies. See references for further details.

Table 3 - PAH content of bitumen and bitumen fumes

Deygout (2010) measured non-methane volatile organic compounds in the emissions of storage tanks holding three types of asphalt (blown asphalt, visbreaker-cracked residue, and straight-run asphalt). The results are given here:

Table 4. Main identified NMVOC categories (mass %).

Binder type	H ₂ S/SO ₂	Thiophenes and disulfides	BTEX	Other monoaromatics	Alkanes	Alkenes	Other compounds
OB	2	7.1	6.1	1.2	59.2	20.7	3.7
CR	0.1	13.5	13.9	2.8	45.6	14.8	9.3
SR	0.8	7.9	12.5	1	51.3	23.8	2.7

BTEX, benzene, toluene, ethylbenzene, and xylene.

In this table, OB is oxidized asphalt, CR is visbreaker-cracked residue, and SR is straight-run asphalt.

Deygout (2010) did not find diaromatics such as naphthalene or polyaromatics in his asphalt storage tank steam vent samples. He found that the vapors vented from the top of the tank were of different composition than the vapors near the surface of the asphalt, so that the composition of the headspace in the tank is not homogenous, with heavier compounds such as diaromatics and polyaromatics staying near the surface of the asphalt.

It is important to remember that speciation in the vapor over a liquid mixture varies with temperature. Deygout (2010) provides tank temperature information.

Capacity, stocks, and throughput

The US EPA’s refinery information collection request (US EPA not dated) asked for annual production of “Asphalt and Road Oil.” These values are given in the “products produced” worksheet of the supplementary Excel workbook titled “component 1 Texas refinery details sanitized.xlsx.” However, all but two of the annual production fields for this product are blank, presumably because of confidential business information. One of the two refineries (#13) reported “Asphalt and Road Oil” production as zero and is excluded from further analysis.

Thirteen refineries (not including #13) list “Asphalt and Road Oil” as a product but only one provides an annual production value: refinery #xxx reports production in 2010 of 719,514 bbl. Four of the 14 refineries in this group provided information about how this stream was transferred offsite (none reported use onsite). Four refineries (#xxx, #6, #2, and #22) report offsite shipping modes. The remaining nine refineries (#21, #19, #16a, #16b, #8, #11, #14, #7and #17), report zeroes and and/or blanks in all of the onsite usage and off-site transfer fields.

The US EPA’s refinery information collection request (US EPA not dated) also includes data on throughput by tank. The supplementary Excel workbook titled “component 1 intermediate storage tanks Texas with corrected tank ids with STARS heat info sanitized.xlsx” includes information about storage tanks at refineries in Texas holding “Asphalts and Road Oils.” A total of 30 tanks were reported to be holding asphalt and road oil (note that in the case of PMB some interpretation was required when determining which tanks held asphalt and road oil).

Reported throughput volumes vary widely amongst the stream categories. Average, maximum, and minimum throughputs for each of the gas oil stream categories are given in the table below.

Stream category	Throughput per tank in 2009, bbl				number of tanks in sample
	average	standard deviation	max	min	
Asphalt and Road Oil	276,653	371,601	1,510,854	4,938	18
Asphalt (AC-5)	25,537	13,879	50,820	7,546	11
PMB*	0	n/a	n/a	n/a	1

*This acronym is not spelled out in the refinery information collection request data, but PMB probably stands for polymer-modified bitumen.

Note that one tank was reported to have a throughput of 0 and that throughput is available for all 30 tanks reported to be holding asphalt and road oil.

The production capacity for asphalt might help to provide a sense of the potential volume of the production of asphalt. Information about the production capacity of asphalt is contained in two of the supplementary Excel workbooks described in the section titled “Refineries in Texas.” One source of capacity information is data collected from US EPA’s refinery information collection request (US EPA not dated) and can be found in the “processes at refineries” worksheet in the “component 1 Texas refinery details sanitized.xlsx” workbook. Refineries in this workbook are identified by number. Data from Koottungal (2013) were used to create another supplementary Excel workbook that gives production capacities for asphalt as of January 1, 2014. The refineries in this workbook are identified by number and by region (inland or Gulf Coast).

This table shows the values for asphalt production capacity from both sets of data.

refinery #	Asphalt, production capacity in barrels per calendar day	
	Koottungal 2013 (values as of Jan 1, 2014)	US EPA not dated (values for 2010)
1	0	0
2	8,000	30,000
3	0	0
4	0	0
5	0	0
6	0	0
7	0	0
8	0	0
9	0	0
10	0	0
11	0	0
12	0	0
13	0	0
14	0	0
15	1,667	8,346
16	38,000	10,800
17	0	0
18	0	0
19	0	16,401
20	0	0
21	0	0
22	4,800	CBI
23	0	0
xxx	No data	0
Total all	52,467	¹

Notes: CBI=confidential business information

¹No totals are given here because they would be distorted by the missing information from refineries with confidential business information claims.

Koottungal (2013) reports no asphalt production capacity at refinery #19, but US EPA (not dated) reports production capacity at this refinery of 16,401 bbl/calendar day in 2010. In general, there is not good agreement between the two sets of data for this stream. Note that the only refinery (#xxx) that reported production of “Asphalt and Road Oil” in the “products produced” tab of the “component 1 Texas refinery details sanitized.xlsx” workbook did not report any “Asphalt production” capacity in the “processes at refineries” tab in that workbook.

Data about the month-to-month change in stored quantities of asphalt may shed light on tank turnover rates as well. The US Energy Information Administration (US EIA) tracks information about refinery stocks of asphalt and road oil. US EIA data for Texas is divided into Gulf Coast and inland refineries (individual refinery data is not published). The following table shows the most recent 12 months of data. US EIA defines asphalt as a cement-like material containing petroleum-derived bitumen as the

predominant constituent and that is used primarily for road construction. Reported amounts include crude asphalt as well as cements, fluxes, the asphalt content of emulsions (exclusive of water), and petroleum distillates blended with asphalt to make cutback asphalts. US EIA defines road oil as any heavy petroleum oil, including residual asphaltic oil, that is used as a dust palliative and surface treatment on roads and highways (US EIA not dated).

From US EIA (2014h):

Date	Refining District Texas Inland Asphalt and Road Oil Stocks at Refineries (Thousand Barrels)	Refining District Texas Gulf Coast Asphalt and Road Oil Stocks at Refineries (Thousand Barrels)
May-2013	673	480
Jun-2013	583	366
Jul-2013	563	273
Aug-2013	542	296
Sep-2013	486	356
Oct-2013	395	227
Nov-2013	407	304
Dec-2013	450	374
Jan-2014	403	359
Feb-2014	367	288
Mar-2014	355	186
Apr-2014	393	135

Storage tank characteristics

Detailed information about storage tanks was obtained during the US EPA’s refinery information collection request (US EPA not dated). The supplementary Excel workbook titled “component 1 intermediate storage tanks Texas with corrected tank ids with STARS heat info sanitized.xlsx” includes information about storage tanks at refineries in Texas holding “Asphalt and Road Oil.” This includes type of tank, dimensions, average storage temperature, types of rim seals, how many times the roof was landed (for floating roof tanks) and what type of controls were used the last time the tank was degassed. This information may reveal whether the same tank was used for more than one product. There is no information about insulation or type of heater used for heated tanks.

A total of 30 tanks were reported to be holding asphalt and road oil (note that in the case of “PMB” some interpretation was required when determining which tanks held asphalt and road oil).

Nearly all of the tanks holding asphalt are fixed-roof, a third of which are vented to a control device. Tank types for each stream category are given in the following table.

Stream category	Number of tanks				
	Fixed roof tank vented to atmosphere	Fixed roof tank vented to control device	Fixed roof tank using vapor balancing	Cone roof tanks	Total
Asphalt and Road Oil	15	2	1	0	18
Asphalt (AC-5)	3	8	0	0	11
PMB*	0	0	0	1	1

*This acronym is not spelled out in the refinery information collection request data, but PMB probably stands for polymer modified bitumen.

Average, maximum, and minimum tank sizes for each of the stream categories are given in the table below.

Stream category	Number of tanks in sample	Tank capacity, ft ³			
		average	standard deviation	max	min
Asphalt and Road Oil	6	216,461	138,714	361,100	14,771
Asphalt (AC-5)	11	26,274	16,272	54,950	10,303
PMB*	0	No data			

*This acronym is not spelled out in the refinery information collection request data, but PMB probably stands for polymer modified bitumen.

For the 17 asphalt storage tanks with both capacity and throughput data, the average throughput:capacity ratio was 1.5 bbl of throughput/ft³ of capacity (standard deviation of 1.0 bbl of throughput/ft³ of capacity).

Average, maximum, and minimum temperatures for each of the stream categories are given in the table below.

Stream category	Temperature, °F				number of tanks in sample
	average	standard deviation	max	min	
Asphalt and Road Oil	318	109	400	87	18
Asphalt (AC-5)	330	0	330	330	11
PMB*	70	n/a	n/a	n/a	1

*This acronym is not spelled out in the refinery information collection request data, but PMB probably stands for polymer modified bitumen.

All of the tanks identified as “Asphalt (AC-5)” were at refinery #15. Tank temperatures below 330°F were reported for only four of the 30 tanks.

According to Deygout (2010), asphalt storage tanks can be free vented or blanketed with an inert (such as steam), depending on the temperature of the stored asphalt. References to steam blanketing of

asphalt storage tanks in order to prevent the presence of explosive vapor outside of the United States are common but the details of asphalt storage tank configurations in the United States were harder to come by and no specific instance of an asphalt storage tank in the United States being steam blanketed was found. In steam blanketing, steam is introduced to the airspace above the asphalt in the tank. In one case, procedures were to feed the steam continuously and vent it continuously if the asphalt in the tank was hotter than 190°C (374°F). At lower temperatures, the steam was introduced and kept heated but not vented (Ferjencik and Janovsky 2010). In another case, three asphalt tanks (one holding straight-run asphalt, one oxidized asphalt, and one visbreaker-cracked residue) were steam blanketed continuously and vented continuously at temperatures between 191 and 205°C (Deygout 2010).

Asphalt storage tanks are heated to keep their contents fluid unless storage is expected to be long term. The minimum pumping temperature, which varies from asphalt to asphalt, is generally the temperature at which the viscosity is 2 Pa-s (Błażejowski et al 2014). Given this guideline and the correlation for calculating viscosities at different temperatures given earlier in this report, if the viscosity of the material in the tank is known at any temperature, the temperature that results in a viscosity of 2 Pa-s would provide a general idea of the minimum temperature of the tank, unless storage was expected to be long term. A more complete explanation of the calculations involved is given in the section on methods for estimating emissions from storage tanks.

Read and Whiteoak (2003) state that asphalt stored in a tank with no fresh asphalt added to it for more than a week should be kept at a temperature of 20 to 25°C above the softening point of the asphalt. Again, this temperature varies from asphalt to asphalt.

This table gives recommended storage temperatures for asphalt of different grades (Nynas 2012):

Appendix 6 - Bitumen storage and handling temperatures (as recommended by Eurobitume)

The table gives an overview of best practice for handling each grade:

PAVING GRADE BITUMEN						
		10/20	15/25	20/30	30/45	35/50
Minimum pumping temperature	°C	150	145	140	130	130
Typical storage temperature	°C	175 - 190	175 - 190	165 - 185	160 - 180	155 - 175
Maximum handling/storage temp	°C	200	200	200	200	200

PAVING GRADE BITUMEN						
		40/60	50/70	70/100	100/150	160/220
Minimum pumping temperature	°C	125	125	120	115	110
Typical storage temperature	°C	150 - 170	145 - 165	140 - 160	135 - 155	130 - 150
Maximum handling/storage temp	°C	200	200	190	190	190

PAVING GRADE BITUMEN					
		250/330	330/430	500/650	650/900
Minimum pumping temperature	°C	100	95	90	85
Typical storage temperature	°C	125 - 145	120 - 140	115 - 135	110 - 130
Maximum handling/storage temp	°C	190	180	170	160

OXIDISED BITUMEN			
		R&B <100°C	R&B >100°C
Minimum pumping temperature	°C	r&b + 80	r&b + 90
Typical storage temperature	°C	200 - 220	210 - 230
Maximum handling/storage temp	°C	230	230

SOFT BITUMEN					
		V1500	V3000	V6000	V12000
Minimum pumping temperature	°C	60	65	70	80
Typical storage temperature	°C	80 - 130	85 - 135	90 - 140	100 - 150
Maximum handling/storage temp	°C	130	140	150	150

According to this table, paving grade asphalt is typically stored at temperatures between 110 and 190°C (230 and 374°F), while oxidized asphalt is stored at temperatures between 200 and 230°C (392 and 446°F), and soft asphalt is stored at temperatures between 80 and 150°C (176 and 302°F). Literature from a supplier of heating systems for asphalt storage tanks describes a storage terminal where the asphalt in the tanks is maintained at 275-350°F (Fulton not dated).

To save on heating costs and preserve asphalt quality, tanks are generally insulated. Tanks are often mixed to maintain uniform temperatures throughout the asphalt. As with heating, it is recommended that mixing be discontinued when storage is long-term (Read and Whiteoak 2003).

The preferred storage temperature for AC-5 (a paving grade asphalt) is 135°C to 163°C (275°F to 325°F). Unnecessarily high temperatures result in increased hardening and heating costs. This asphalt must be stored in insulated tanks, which have hot oil, electric or high-pressure steam heating systems (US Oil and Refining not dated).

No instances of the use of direct contact steam to heat asphalt in storage tanks were found.

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5. Coker naphtha

Stream origins and destinations

Coking is a form of thermal cracking, along with visbreaking and steam cracking. Primary coker feeds are FCC residuum and straight run residual oil. Coker naphtha is an example of a cracked naphtha, which contains olefins. Cracked naphthas can also be produced from visbreakers and fluid catalytic crackers. They are low quality naphthas and are usually treated the same as heavy naphthas – hydrotreated and/or sent to desulfurization and catalytic reforming before being blended into gasoline. Coker light naphtha is sometimes fed to an isomerization unit (Gary et al 2007).

Physical properties of streams

Initial boiling point, final boiling point, density, and an intermediate distillation temperature are given here.

From Lengyel et al (2009):

Table 1. Typical characteristics of delayed coker light naphtha fractions

Characteristics	Values
Density (15°C), g/cm ³	0.650-0.680
Sulphur content, mg/kg	5000-20000
Nitrogen content, mg/kg	50-300
Research octane number (RON)	80-90
Motor octane number (MON)	70-80
Hydrocarbon composition, vol%	
paraffins	40-50
olefins	30-50
diolefins	1-2
naphthenes	5-10
aromatics	0.5-2
Distillation (ASTM D86), °C	
initial boiling point	25-35
95 vol%	65-80
final boiling point	75-85
Bromine number, g Br/100g	20-100
Silicon content, mg/kg	1-20

This table also includes data on average molecular weight and additional distillation fractions. From Lengyel et al (2010):

Table 1
Main characteristics of hydrocarbons cuts

Characteristics	Hydrocarbon feedstocks		
	A	B	C
	10% DCLN + 90% LSRN	20% DCLN + 80% LSRN	5% DCLN + 95% FCC gasoline
Density (15°C), g/cm ³	0.675	0.684	
Sulfur content, mg/kg	433	746	525
Nitrogen content, mg/kg	8	15.8	35
Silicon content, mg/kg	69	140	
Bromine number, g Br/100 g	11	18	
Average molecular weight	81.74	81.17	94.7
HC composition, wt%			
Naphthenes	20.25	18.28	9.2
Paraffins	72.98	71.87	37.4
Olefins	5.41	8.69	23.2
Aromatics	1.36	1.16	30.2
Diolefin content, %	0.20	0.40	—
Diolefin composition, wt%			
Isoprene	0.03	0.06	0.046
1-trans-3-Pentadien	0.05	0.09	0.047
1,3-Cyclopentadien	0.00	0.00	0.00
1-cis-3-Pentadien	0.04	0.07	0.041
2,3-Pentadien	0.01	—	0.002
Total C ₅ diolefins	0.13	0.22	0.136
Simulated distillation			
IBP, °C	−6	−6	2
10%, °C	23	23	24
30%, °C	36	36	62
50%, °C	61	61	98
70%, °C	75	75	116
90%, °C	94	93	188
95%, °C	103	98	206
FBP, °C	118	117	232

Note that in the latter table, DCLN is delayed coker light naphtha and LSRN is light straight run naphtha. (Per Koottungal (2013), nearly 90% of the coker capacity in Texas is delayed cokers.) The coker naphtha and the light straight run naphtha have similar molecular weights and densities (81-82 g/mol and 0.675 to 0.684, respectively). Also, the simulated distillation temperatures for coker naphtha and light straight run naphtha are similar until temperatures approach their final boiling point.

Composition of streams

Cracked naphthas have linear and cyclic olefins and di-olefins. They cause problems in the upgrading units because of the olefins and sulfur/nitrogen content (0.4–2% sulfur, 40–400 ppmw nitrogen, 1–2% diolefins, 35–45% olefins) (Lengyel et al 2010).

Some composition data is given in the previous table from Lengyel et al (2009). In addition, the speciated diolefin concentrations of the coker naphtha could be derived from the DCLN+LSRN data

columns in the Lengyel et al (2010) table in the previous section. This table shows that the hydrocarbon composition is similar for coker naphtha and light straight run naphtha except for the olefins and diolefins. Coker naphtha also has fewer aromatics than light straight run naphtha.

Capacity, stocks, and throughput

It may be that coker naphtha generation can be tied to coking capacity or production of coke at refineries. The US EPA refinery information collection request gathered data on cokers (US EPA not dated). The capacities of 14 delayed cokers and the coke production of 12 delayed cokers at refineries in Texas is given by refinery in the supplementary Excel workbook titled “component 1 cokers Texas sanitized.xlsx.”

The Energy Information Administration (US EIA) tracks the production of coke by year by Texas region (US EIA 2014c and 2014d). These data can be found in two supplementary Excel workbooks (Texas Gulf coast refinery net production.xlsx” and “Texas inland refinery production.xlsx.”) Capacity for some of the processes that treat or create intermediate streams of interest at individual refineries in Texas is available in the 2014 Worldwide Refining Survey (values as of January 1, 2014) (Koottungal 2013). These data include coking capacity and are provided in the supplementary Excel workbook “Texas refinery unit capacities 2014.xlsx.”

Most refineries that generate cracked naphtha minimize storage because of its tendency to polymerize. Stocks are expected to be low.

Storage tank characteristics

Cracked naphthas have a tendency to polymerize when contacted with oxygen, which causes fouling in upgrading processes. Most refineries minimize their storage or blanket them when stored. In the data from the US EPA’s refinery information collection request (US EPA not dated), tanks storing coker naphtha might have been reported with “Unfinished Oils – Naphthas and lighter” as the stored liquid. None of the tanks in the dataset identified coker naphtha specifically as their stored liquid, so it is impossible to tell if any refineries in Texas are storing coker naphtha in tanks.

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6. Reformate

Stream origins and destinations

Reformate is the product of catalytic reforming, which is usually conducted to boost the octane number of fuels.

Physical properties of streams

No literature values were found for properties of reformate.

Composition of streams

The composition of 12 reformate streams can be found in Job et al (1996):

Table 1 PONA composition (vol.%) of samples used for developing correlation

Sample no.	Paraffins	Olefins	Naphthenes	Aromatics
1	28.2	1.8	1.4	68.6
2	30.7	1.9	1.0	66.4
3	31.7	1.1	0.8	66.4
4	32.1	0.6	0.5	66.8
5	33.5	0.3	0.7	65.5
6	34.6	0.6	0.6	64.2
7	34.8	0.7	0.7	63.8
8	35.2	1.3	1.3	62.2
9	37.9	1.1	1.2	59.8
10	38.2	0.9	1.0	59.9
11	46.9	0.9	1.4	50.8
12	53.2	0.8	2.9	43.1

Capacity, stocks, and throughput

The US EPA's refinery information collection request (US EPA not dated) includes data on throughput by tank. The supplementary Excel workbook titled "component 1 intermediate storage tanks Texas with corrected tank ids with STARS heat info sanitized.xlsx" includes information about four refineries in Texas with eight storage tanks that appear to be holding reformate (note that in the case of "UDEX charge" some interpretation was required when determining this tank holds reformate).

Throughput was available for seven of the eight tanks, and average throughput was 1,400,496 bbl in 2009 with a standard deviation of 1,079,068 bbl.

The throughput capacities of reformers at refineries in Texas might help to provide a sense of the potential volume of the production of reformate. Information about the process capacities of reformers is contained in two of the supplementary Excel workbooks described in the section titled "Refineries in Texas." One source of capacity information is data collected from US EPA's refinery information collection request (US EPA not dated) and can be found in the "processes at refineries" worksheet in the "component 1 Texas refinery details sanitized.xlsx" workbook. Refineries in this workbook are identified by number. Data from Koottungal (2013) were used to create another supplementary Excel workbook that gives catalytic reforming capacities as of January 1, 2014. The refineries in this workbook are identified by number and by region (inland or Gulf Coast).

This table shows the values for reforming throughput capacity from both sets of data.

refinery #	Catalytic reforming throughput capacity in barrels per calendar day	
	Koottungal 2013 (values as of Jan 1, 2014)	US EPA not dated (values for 2010)
1	0	5,300
2	21,000	21,000
3	124,300	CBI
4	45,450	47,000
5	33,800	37,528
6	17,500	17,500
7	120,000	CBI
8	138,500	CBI
9	66,600	69,673
10	33,700	36,000
11	10,500	10,000
12	45,000	45,000
13	20,000	CBI
14	67,100	69,500
15	37,918	39,600
16	47,000	49,000
17	0	0
18	53,000	55,000
19	47,400	46,000
20	14,500	37,100
21	34,000	33,500
22	18,000	26,000
23	29,000	CBI
xxx	No data	0
Total all	1,024,268	¹

Notes: CBI=confidential business information

¹No totals are given here because they would be distorted by the missing information from refineries with confidential business information claims.

Stocks of reformate may be difficult to assess.

Storage tank characteristics

Detailed information about storage tanks holding intermediates was obtained during the US EPA’s refinery information collection request (US EPA not dated). The supplementary Excel workbook titled “component 1 intermediate storage tanks Texas with corrected tank ids with STARS heat info sanitized.xlsx” includes information about eight storage tanks at refineries in Texas holding liquids specified as reformate or UDEX feed. This includes type of tank, dimensions, average storage temperature, types of rim seals, how many times the roof was landed (for floating roof tanks) and what type of controls were used the last time the tank was degassed. This information may reveal whether the same tank was used for more than one product. There is no information about insulation or type of heater used for heated tanks.

Three of the tanks were external floating roof tanks, four were internal floating roof tanks, and one was a cone roof tank.

Capacity could be calculated for only two of the tanks; the average capacity was 441,563 ft³. The throughput:capacity ratio could be calculated for only one of the tanks and was 3.7 bbl of throughput per ft³ of capacity.

The average temperature of the eight tanks was 80°F, with a standard deviation of 12°F. Reported temperatures ranged from a high of 95°F to a low of 70°F.

Literature

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US Environmental Protection Agency (US EPA). December 7, 2012. High production volume (HPV) chemical challenge program, Robust summary of information, Heavy fuel oil category. 201-16879B.

7. Pyrolysis gasoline

Pyrolysis gasoline is also sometimes called pygas, debutanized aromatic concentrate, or high benzene naphtha. After hydrogenation it is known as hydrogenated pyrolysis gasoline (HPG) or BTX.

Stream origins and destinations

Pyrolysis gasoline is a byproduct of olefin production when olefins are produced by steam cracking. It can be blended into gasoline or distilled to separate the aromatics it contains. Sometimes the stream is hydrogenated before distillation.

Physical properties of pyrolysis gasoline

Further work is needed to identify the properties of pyrolysis gasoline.

Composition of streams

Pyrolysis gasoline is high in aromatics and may contain isoprene, benzene, toluene, and the xylenes.

Hansen (2014) provides two breakdowns of liquid constituents in “Pyrolysis Gas (PYE Gas).” The first breakdown is:

Compound	Wt %
3-Methyl-1-butene	0.33
Isopentane	3.10
1,4 Pentadiene	0.33
1-Pentene	1.14
2-Methyl-1-butene	1.12
Pentane	1.47
Isoprene (2-methyl-1,3-butadiene)	2.54
trans-2-Pentene	0.88
cis-2-Pentene	0.49
2-Methyl-2-butene	0.67
trans 1,3 Pentadiene	1.43
Cyclopentadiene	1.42
C5s-IP, CPD*	13.09
cis 1,3 Pentadiene	0.85
Cyclopentene	0.97
Cyclopentane	0.26
Benzene	23.63
Toluene	10.47
Dicyclopentadiene	1.57
C11s plus	8.68
C7s thru C10s+ [#]	41.24
Total C4s and lighter	0.73

*The meaning of IP and CPD is not spelled out in the source, but the intent of this line may be to include C5s except for isoprene and cyclopentadiene; the analysis method is not given but it may instead mean C5s eluted (or whatever parallel mechanism applies) up to and including isoprene and cyclopentadiene.

[#]It may be that the plus sign here is unintended or it may be that “C11s plus” is included in this line.

Note that the total may not equal 100% (the C4s and lighter; C5s-IP, CPD; isoprene; cyclopentadiene; benzene; C7s thru C10s+; and C11s plus add up to 91.33%). It is noted that there are no C6 alkanes listed and the total for the C5s that are individually listed add up to more than the sum of the C5s-IP, CPD; isoprene; and cyclopentadiene lines. The sum of the all the values excluding the rows above the C5s-IP, CPD entry is 101.49%.

The second breakdown (Hansen 2014) is:

Compound	Wt %
Ethylbenzene	0.0008
Styrene (phenylethene)	0.0008
p-Xylene	0.0008
2-Methylpentane	0.0158
m-Xylene	0.0008
Toluene	0.071
n-Pentane	0.0742
1-Pentene	0.0148
n-Hexane	0.0396
Cyclohexane	0.0158
Cyclopentene	0.0089
n-Heptane	0.0403
Piperylene (1,3-pentadiene)	0.0744
1,3-Cyclopentadiene	0.0728
2-Methyl-1-butene	0.0327
Isobutane	0.0075
Dicyclopentadiene	0.0008
Isopentane	0.0594
Isoprene (2-methyl-1,3-butadiene)	0.105
o-Xylene	0.0008
TOTAL	0.637

The total for all the compounds in this table is 0.637. A comparison of compounds that appear in both sets of data (e.g., 1-pentene, 2-methyl-1-butene, cyclopentene, dicyclopentadiene, isopentane, toluene, 1,3-pentadiene) makes it seem likely that the values in the latter set of data are weight fractions, not weight %. None of the compounds in the second table has more than 8 carbon atoms.

Capacity, stocks, and throughput

Capacity for this stream may be difficult to determine. None of the processes identified in the data gathered as a result of the US EPA's refinery information collection request (US EPA not dated) mention pyrolysis gasoline or steam cracking. Olefins are produced by processes other than steam cracking at refineries, so it is unlikely that that pyrolysis gasoline generation can be tied to olefin capacity or production of olefins at refineries. Pyrolysis gasoline is also not the only source of aromatics.

However, in the supplementary Excel workbook titled "component 1 intermediate storage tanks Texas with corrected tank ids with STARS heat info sanitized.xlsx," throughput is given for three tanks holding

pygas at refinery #15. Reported throughputs for these tanks are 814,578, 11,112, and 494,728 bbl in 2009. The stored liquid descriptions for these three tanks are Pygas, PFO/PGO, and PFO/PGO X.XX.

Stocks may also be difficult to assess.

Storage tank characteristics

Detailed information about storage tanks holding intermediates was obtained during the US EPA's refinery information collection request (US EPA not dated). The supplementary Excel workbook titled "component 1 intermediate storage tanks Texas with corrected tank ids with STARS heat info sanitized.xlsx" includes information about three storage tanks at a refinery in Texas holding liquids specified as pygas. This includes type of tank, dimensions, average storage temperature, types of rim seals, how many times the roof was landed (for floating roof tanks) and what type of controls were used the last time the tank was degassed. This information may reveal whether the same tank was used for more than one product.

One of the tanks was an external floating roof tank and the other two were fixed roof using vapor balancing.

Capacities of the three tanks were 593,725, 395,640, and 429,552 ft³. Throughput:capacity ratios were 1.4, 0.028, and 1.2 bbl of throughput per ft³ of capacity.

Storage tank temperatures were 91.9, 60.3, and 150°F.

Literature

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8. Residuum

An MSDS for refinery #10 (Refinery #10 2006h) lists the following synonyms for carbon black oil: CBO, catalytic cracked clarified oil (petroleum), clarified oil, claroil, clarified slurry oil, cat slurry oil, fluid catalytic cracker unit (FCCU) residuum, FCCU decant oil, FCCU claroil, bottoms stream from a fluid catalytic cracker unit, FCCU bottoms, 732 unit bottoms, coker feed component, No. 6 fuel oil blending component, heavy fuel oil blending component, carbon black unit feedstock, unfinished bunker fuel, C20-C50 petroleum hydrocarbons.

Stream origins and destinations

Residuum is a general term for material left over after distillation or other purification processes that drive off lighter liquids. It is generated from various processes throughout refineries.

The major residuum stream at most refineries is the residuum from atmospheric distillation, which at most refineries is sent to vacuum distillation. The residue from vacuum distillation is usually the second largest residual stream at a refinery; when a high-asphalt crude is fed, this stream would be further processed to make asphalt for roads and roofing. More information about these two residuum streams can be found in the "Atmospheric and vacuum bottoms" section of the report.

Nearly every upgrading process generates residuum. Possible fates of other residuum streams include being routed to atmospheric or vacuum distillation or sent to coking. At the present time, most heavy fuel oils (residual fuels) consist primarily of vacuum tower residues and residues from thermal and catalytic cracking (US EPA 2004). In fact, the American Petroleum Institute's definition of heavy fuel oil is, in part "the liquid product from various refinery streams, usually residues" (US EPA 2004). To lower the viscosity into a desirable heavy fuel oil range (such as No. 6 fuel oil), the residual streams are mixed with cutter stock. This cutter stock could be any one of a number of low value distillate streams and would vary from refinery to refinery as well as from time to time within the same refinery.

Physical properties of streams

The vapor pressure at the average storage tank temperature (along with that temperature) are given for "Unfinished Oils – Residuum" in 25 storage tanks in Texas in the supplementary Excel workbook titled "component 1 intermediate storage tanks Texas with corrected tank ids with STARS heat info sanitized.xlsx." It is not possible to discern which of these tanks hold vacuum and tower bottoms and which hold other residues. There are also some storage tanks whose contents were described as "other" that could contain residues other than atmospheric and vacuum tower bottoms.

Physical properties of four residual streams can be found in Singh et al (2004): North Gujarat vacuum residue (NGSR), Bombay High vacuum residue blended with oil fluxes (BHSR), visbreaker feed from the Mathura refinery (MVBF), and asphalt feedstock from the Haldia refiner (HRA). The characterization of these streams is:

Table 1
Feed characteristics

S.N.	Characteristic-parameter	Feed			
		MVBF	HRA	BHSR	NGSR
1	Merit number	2.5	2.0	—	—
2	<i>n</i> -C ₅ insolubles, wt%	13.19	26.92	7.25	11.24
3	<i>n</i> -C ₇ insolubles, wt%	8.9	12.70	4.46	2.11
4	Asphaltenes, wt%	7.72	10.15	3.03	1.85
5	Pour point, °C	+39	+72	+69	+48
6	Metals (elements mg/l)				
	V	29.3	95.75	3.4	43.00
	Ni	36.55	46.3	24.95	167.15
	Fe	22.90	30.80	8.3	19.30
7	Density D ₄ ¹⁵	1.0176	1.0542	0.9636	0.9887
8	Kin. viscosity, cSt at 100 °C	526.5	8217.3	91.3	1522.0
9	Kin. viscosity, cSt at 135 °C	102.3	690.7	24.4	288.83
10	Sulfur, wt%	4.29	4.93	0.45	0.28
11	CCR, wt%	19.8	25.7	12.8	15.36
12	C/H ratio	7.50	7.78	5.58	7.85
13	Molecular weight	871.2	1078.8	793.5	—
14	Hydrocarbon type				
	Saturates	14.76	5.63	32.89	10.3
	Aromatics, naphthenic	67.85	68.07	59.82	58.71
	Polar	6.40	11.86	4.23	29.20
	<i>n</i> -C ₇ insolubles	10.47	13.69	4.46	2.11

The US EPA (2012) reports the boiling point range of catalytic reformer fractionator residues at 160-400°C and the boiling point range of catalytic reformer fractionator residue residues (this is not a typo) at >399°C, while hydrocracked and thermal cracked residues have a boiling point range that is >350°C. This source reports that heavy coker gas oil and vacuum gas oil residues have boiling point ranges >230°C and coker scrubber condensed-ring aromatic-containing residues have a boiling point range >350°C.

The carbon black oil MSDS for refinery #10 (Refinery #10 2006h) gives the boiling point range of this stream as 270-600°C (520-1,110°F) and the melting point range is 21-30°C (70-86°F). The specific gravity at 60°F is 1.00-1.09. The vapor pressure is given as < 0.01 mm Hg at 21°C (70°F) and the viscosity is given as 11.6-15.5 cSt at 100°C.

Stratiev and others (2008) provide information about several physical properties of FCC slurry:

Property	FCC slurry 1	FCC slurry 2	FCC slurry 3
Density at 20°C, g/cc	1.049	0.9862	1.0726
Distillation ASTM D-2887, °C			
IBP	206	178	196
5%	262	200	296
10%	278	214	321
30%	324	267	359
50%	366	325	386
70%	404	371	417
90%	459	426	469
95%	483	452	493
FBP	533	504	538
Molecular weight*	233	210	248
Refraction, nd20	1.6248	1.5783	1.6511
Temperature, °C.	Viscosity, sq mm/sec		
20		22.47	
30			
40	107.77	9.56	194
50	46.3		85.14
60	29.8		44.83
70	20.01		25.62
80	14.52	3.56	16.18

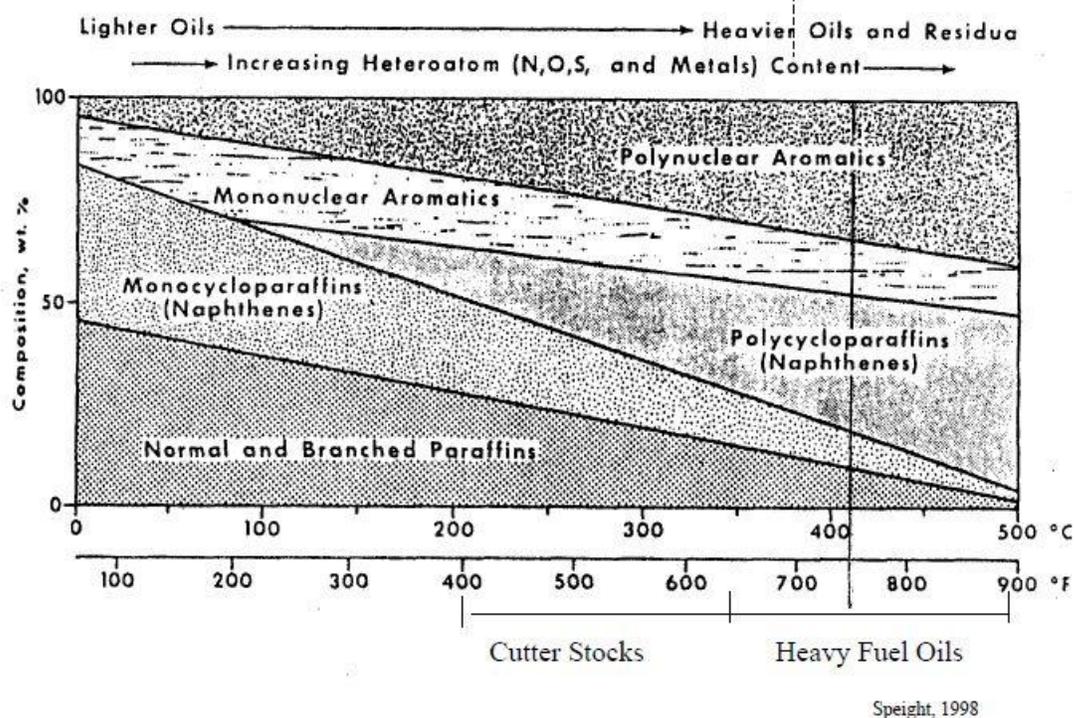
*Stratiev and others (2008) report that this value was estimated using Goossens 1993.

Composition of streams

The composition of residual streams would differ depending on the process from which they arose. These streams usually contain suspensions of resin/asphaltene complexes and often have high levels of heterocyclic aromatic (with sulfur, nitrogen, oxygen, and other elements present) and naphthenic compounds (US EPA 2004). The polyaromatic hydrocarbon content of these streams is often more than 5%, but depending on the processing the stream has undergone, it can be much higher than 5% (US EPA 2004). According to US EPA (2004), a representative sample of cracked residue is 58% aromatics.

US EPA (2004) modified the following figure from an earlier edition of Speight's petroleum handbook to show where cutter stock and residuum for heavy fuel oils fall in the continuum of refinery stream composition:

Figure 2. Refinery Stream Composition – Boiling Range vs. General Composition



Residues from cracking processes tend to have more aromatics and olefins than straight-run residues (US EPA 2004).

The MSDS for carbon black oil for refinery #10 (Refinery #10 2006h) gives the composition of carbon black oil as 50-90% C₂₀-C₅₀ saturated hydrocarbons and naphthenes; 10-50% polynuclear aromatic hydrocarbons (4- to 6-member condensed-ring type); 0.1-0.3% 5-methylchrysene; 0.1-0.2% chrysene (benzo[a]phenanthrene); 0.05 to 0.15% benzo[a]anthracene; and 0.001 to 0.01% hydrogen sulfide. The list of compounds found in the workplace exposure section of this MSDS may provide clues about the compounds present in the stream. This list is: hydrogen sulfide; oil mist, mineral; coal tar pitch volatiles, as benzene solubles ("A1" confirmed human carcinogen); and oil mist, mineral, sum total of 15 PAHs listed as carcinogens by US NTP. (Note that the 15 PAHs listed by US NTP (2011) are benz[a]anthracene, benzo[b]fluoranthene, benzo[j]-fluoranthene, benzo[a]pyrene, dibenz[a,h]acridine, dibenz[a,j]acridine, dibenz[a,h]anthracene, 7H-dibenzo[c,g]-carbazole, dibenzo[a,h]pyrene, dibenzo[a,i]pyrene, indeno[1,2,3-cd]pyrene, benzo[k]fluoranthene, dibenzo[a,e]pyrene, dibenzo[a,l]pyrene, and 5-methylchrysene.) This MSDS does not give a workplace exposure level for chrysene (benzo[a]phenanthrene) or benzo[a]anthracene, but lists them separately in the occupational exposure guidelines section. Under "volatile characteristics," this MSDS says "Negligible, no volatile organic compounds (VOCs) present at 500°F."

Stratiev and others (2008) give some composition data for FCC slurry:

Property	FCC slurry 1	FCC slurry 2	FCC slurry 3
Composition, %			
Saturates	14.4		
Monoaromatics	0.8		
Polyaromatics	80.8		
Olefins			
Resins	3.2		
Asphaltenes	0.8		
Sulfur, %	0.3	0.3	0.3
Hydrogen, % (estimated using a correlation)	6.9	8.4	5.9

Capacity, stocks, and throughput

The US EPA’s refinery information collection request (US EPA not dated) asked for annual production of “Unfinished Oils – residuum.” These values are given in the “products produced” worksheet of the supplementary Excel workbook titled “component 1 Texas refinery details sanitized.xlsx.” However, many of the quantity fields are blank, presumably because they were confidential business information. This data would be expected to contain information about both distillation tower bottoms and other residuum, and many of the lines of data (but not all) in the analysis for the “Atmospheric and vacuum tower bottoms” section are shared with the lines of data in this section’s analysis.

Sixteen refineries list “Unfinished Oils – Residuum” as a product but only one provides an annual production value: refinery #13 reports production in 2010 of 275,000 bbl. Seven of the 16 refineries in this group provided information about whether this stream was used onsite or transferred offsite. Two refineries (#6 and #7) reported that none of the “Unfinished Oils – Residuum” they produce are used onsite, while another two refineries (#4b and #13) report that 100% of this stream is used onsite. One refinery (#11) reported zeroes for all onsite and offsite usage and another refinery (#8) reported 20% shipped by barge with zeroes for other onsite and offsite usage. The remaining refinery (#19) reported 80% onsite usage.

The US EPA’s refinery information collection request (US EPA not dated) also includes data on throughput by tank. The supplementary Excel workbook titled “component 1 intermediate storage tanks Texas with corrected tank ids with STARS heat info sanitized.xlsx” includes information about storage tanks at refineries in Texas holding “Unfinished Oils – Residuum.” Many of the streams in the “other” category are also residual streams other than atmospheric and vacuum distillation tower bottoms. A total of 34 tanks were reported to be holding residuum other than residuum specifically identified as atmospheric and vacuum distillation tower bottoms (note that in a few cases some interpretation was required when determining which tanks held residuum). Five of these tanks held carbon black oil, four held coker feed, and the remaining and the remaining 25 tanks held streams that were not described as “Unfinished oils - Residuum.”

Reported throughput volumes vary widely amongst the stream categories. Average, maximum, and minimum throughputs for each of the gas oil stream categories are given in the table below.

Stream category	Throughput per tank in 2009, bbl				number of tanks in sample
	average	standard deviation	max	min	
Unfinished Oils – Residuum	1,183,222	1,960,650	5,884,476	0	11
Carbon black oil (CBO*)	521,066	520,590	1,424,987	113,814	5
Coker feed (unspecified, heavy, and light)	1,722,290	1,817,593	3,463,546	12,736	4

*This acronym is not spelled out in the refinery information collection request data, but CBO probably stands for carbon black oil.

Note that some tanks were reported to have a throughput of 0 and that throughput is only available for 20 of the 34 tanks holding unspecified residuum other than residuum specifically identified as atmospheric and vacuum distillation tower bottoms.

Data about the month-to-month change in stored quantities of residuum may shed light on tank turnover rates as well. The US Energy Information Administration (US EIA) tracks information about refinery stocks of unfinished oils characterized as residuum. US EIA data for Texas is divided into Gulf Coast and inland refineries (individual refinery data is not published). The following table shows the most recent 12 months of data. US EIA defines “unfinished oils” as all oils requiring further processing, except those requiring only mechanical blending. Residuum is described as residue from crude oil after distilling off all but the heaviest components, with a boiling range greater than 1000°F (US EIA not dated).

From US EIA (2014):

Date	Refining District Texas Inland Residuum Stocks at Refineries (Thousand Barrels)	Refining District Texas Gulf Coast Residuum Stocks at Refineries (Thousand Barrels)
May-2013	543	3,071
Jun-2013	643	2,694
Jul-2013	663	2,864
Aug-2013	648	3,647
Sep-2013	688	2,928
Oct-2013	877	2,898
Nov-2013	624	2,339
Dec-2013	558	2,701
Jan-2014	505	2,396
Feb-2014	485	2,448
Mar-2014	498	2,669
Apr-2014	730	2,344

Note that this table would contain data on atmospheric and vacuum distillation bottoms as well as other residuum stocks and is repeated from an earlier section on atmospheric and vacuum distillation bottoms.

Storage tank characteristics

Detailed information about storage tanks holding residuum was obtained during the US EPA’s refinery information collection request (US EPA not dated). The supplementary Excel workbook titled “component 1 intermediate storage tanks Texas with corrected tank ids with STARS heat info sanitized.xlsx” includes information about storage tanks at refineries in Texas holding “Unfinished Oils – Residuum” (no distinction is made between sources of residuum in this set of data). The information includes type of tank, dimensions, average storage temperature, types of rim seals, how many times the roof was landed (for floating roof tanks) and what type of controls were used the last time the tank was degassed. This information may reveal whether the same tank was used for more than one product. There is no information about insulation or type of heater used for heated tanks. Note that all of the reported residuum storage tanks in Texas had fixed roofs except for one tank identified as holding “heavy coker,” the tank was a cone roof tank. Many of the streams in the “other” category are also residual streams that could perhaps be residuum other than atmospheric and vacuum tower bottoms.

A total of 34 tanks were reported to be holding residuum not otherwise specified as atmospheric and vacuum tower bottoms (note that some interpretation was required when determining which tanks hold residuum). All of these tanks were fixed roof tanks vented to the atmosphere except for one tank holding “heavy coker,” which was a cone roof tank.

Average, maximum, and minimum tank sizes for each of the stream categories are given in the table below.

Stream category	Number of tanks in sample	Tank capacity, ft ³			
		average	standard deviation	max	min
Unfinished Oils – Residuum	25	404,976	384,795	1,372,180	107,388
Carbon black oil (CBO*)	4	189,610	129,025	375,858	84,906
Coker feed (unspecified, heavy, and light)	4	140,159	147,276	267,375	0

*This acronym is not spelled out in the refinery information collection request data, but CBO probably stands for carbon black oil.

For the 18 residuum storage tanks with both capacity and throughput data, the average throughput:capacity ratio was 5 bbl of throughput/ft³ of capacity (standard deviation of 8 bbl of throughput/ft³ of capacity).

Average, maximum, and minimum temperatures for each of the stream categories are given in the table below.

Stream category	Temperature, °F				number of tanks in sample
	average	standard deviation	max	min	
Unfinished Oils – Residuum	113	66	362	75	24
Carbon black oil (CBO*)	166	72	275	73	5
Coker feed (unspecified, heavy, and light)	232	116	320	70	4

*This acronym is not spelled out in the refinery information collection request data, but CBO probably stands for carbon black oil.

As with asphalts, the minimum pumping temperature of residuals would generally be the temperature at which the viscosity is 2 Pa-s (Błażejowski et al 2014). Given this guideline, if the viscosity of the material in the tank is known at any temperature, the temperature that results in a viscosity of 2 Pa-s, which can be calculated using the correlation for predicting viscosities of asphalts and heavy oils at various temperatures, would provide a general idea of the minimum temperature of a tank holding residuum, unless storage was expected to be long term. A more complete explanation of the calculations involved is given in the section on methods for estimating emissions from storage tanks.

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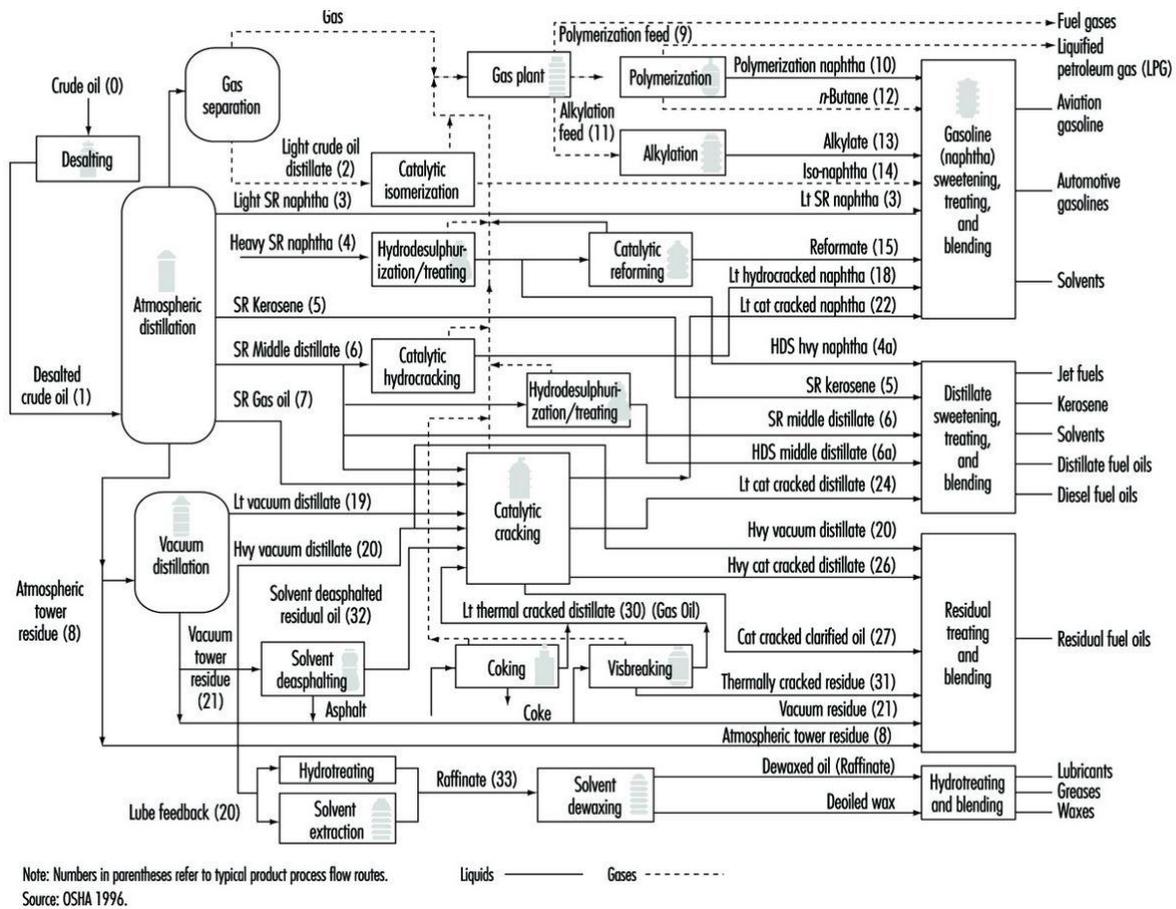
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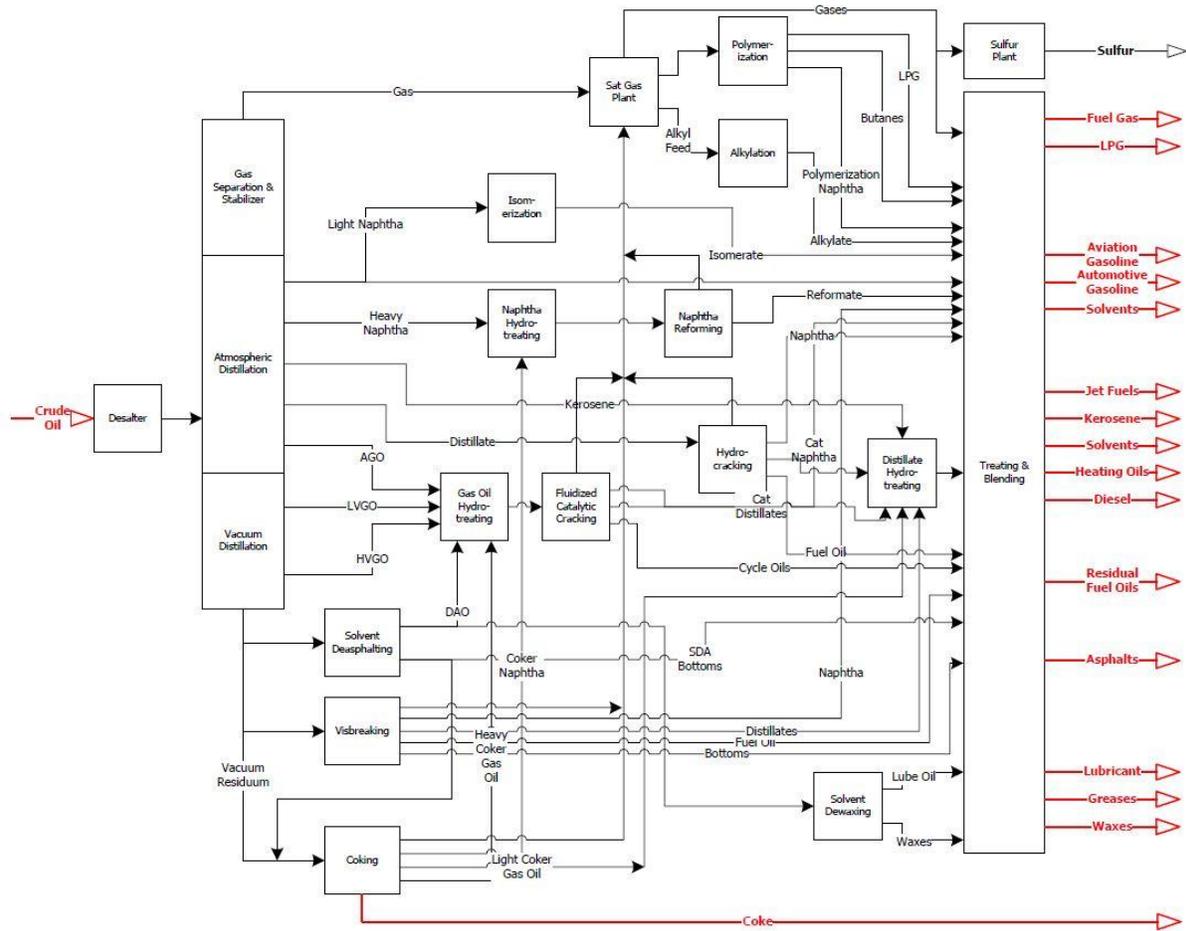
Liquid feedstocks and products of selected refinery processes

In general, naphtha streams are reformed and treated before being blended into gasoline, kerosene and light distillates are treated before being blended into fuels, gas oil from the atmospheric column is sent to catalytic cracking, and residual is sent to vacuum distillation. In practice, refinery processes tend to be interconnected and complicated. Because of the variation in refinery configurations, it is perhaps helpful to review a collection of flow diagrams for the processes of interest in order to develop a sense of what the possible liquid feedstocks and products are.

This figure from the United Nation International Labour Organization (UN ILO) (2011) shows a simplified overall flow diagram at a refinery; many of the processes of interest are present:



Here is another process flow diagram of a refinery (Jechura 2014):



Isomerization unit

The isomerization unit converts straight chain hydrocarbons (butane, pentane, hexane) to branched hydrocarbons (isobutene, isopentane, isohexane), which increases the octane level. The primary feedstock is light straight run naphtha. Often, the feedstock for an isomerization unit has been hydrotreated. Isomerate has no benzene and virtually no sulfur. From Gary et al (2007):

TABLE 10.6
Isomerization Unit Material Balance: 100,000 BPCD Alaska North Slope
Crude Oil Basis (Severity, Once-Through)

Component	vol%	BPD	°API	(lb/hr)/BPD	lb/hr	wt% S	lb/hr
Feed							
C ₅ -180°F	73.4	4,277	63.0	10.61	45,394	0.02	1
Coker light naphtha	26.6	1,551	65.0	10.51	6,303	0.41	64
Total	100.0	5,828			616,970		65
Products							
H ₂ S					69		65
C ₃ , wt%	0.5	29		7.39	215		
iC ₄	0.8	47		8.22	382		
nC ₄	2.2	128		8.51	1,092		
C ₅ + reformat	98.4	5,735	65.6	10.46	60,007		
Total		16,975			204,800		65

S

According to Koottungal (2013), 26% of the isomerization capacity at refineries in Texas is C4 feed, 23% is C5 feed, and 51% is C5 and C6 feed. The total isomerization capacity at refineries in Texas is 109,122 barrels per calendar day.

Catalytic reformer unit

The reformer is used to upgrade low octane naphtha for blending into gasoline. It converts straight run heavy naphtha, coker naphtha, and hydrocracker naphtha into high-octane reformat and aromatics. The feed stock for reformers has to have very low sulfur and has usually been hydrotreated. Reformers produce hydrogen as well as gasoline blendstock. From Gary et al (2007):

TABLE 10.5
Hydrotreater and Catalytic Reformer Material Balance: 100,000 BPCD Alaska
North Slope Crude Oil Basis (Severity, 94 ROM clear; $K_w = 11.7$)

Component	vol%	BPD	°API	(lb/hr)/BPD	lb/hr	wt% S	lb/hr S
Feed							
190–380°F HSR	69.3	12,500	48.5	11.47	143,380	0.1	140
Coker naphtha	30.7	5,540	54.6	11.09	61,420	0.65	400
Total	100.0	18,040			204,800		540
Products							
H ₂ wt%, total	1.7				3,480		
C ₁ + C ₂ wt%	1.0				2,050		
C ₃ , wt%	1.8	500		7.42	3,690		
iC ₄	2.0	360		8.22	2,960		
nC ₄	2.8	505		8.51	4,300		
C ₅ + reformat	86.5	15,610	39.7	12.06	188,320		
Total		16,975			204,800		
Hydrogen^a							
H ₂ S					574		540
H ₂ , net					3,446		

^a H₂S = 32.06 = 16.84 lb-mol/hr; H₂ in H₂S = (16.84)(2) = 34 lb/hr

In this table, HSR is heavy straight run. The residuum from catalytic reforming is sometimes blended into heavy fuel oils (US EPA 2004).

According to Koottungal (2013), 19% of the catalytic reformer capacity at refineries in Texas is shut down at intervals for catalyst regeneration, 28% can regenerate catalyst in one of several reactors while the other reactors continue processing without changing the reformer feed rate or octane, and 53% has catalysts that are continuously regenerated. The total catalytic reforming capacity at refineries in Texas is 1,024,268 barrels per calendar day.

Fluid catalytic cracking (FCC) unit

The primary feeds to FCC units are usually straight run distillate, straight run gas oil, and coker distillate, and the primary outputs are light gases, gasoline blendstock, diesel blendstock, and petrochemical feedstocks. Coker gas oil is another potential FCC unit feed. The main function of an FCC unit is to increase the yield of light products. About a third of the gasoline pool comes from catalytic cracking. The heavier fraction from an FCC unit (the residuum) can be blended into heavy fuel oil (US EPA 2004), fed to a coker, or hydrocracked. FCC feed is often hydrotreated to remove sulfur and the FCC naphtha is often hydrotreated for sulfur removal.

According to Koottungal (2013), 90% of the catalytic cracking capacity at refineries in Texas is fluid catalytic cracking, 5% is non-fluid catalytic cracking, and 5% is unspecified. The total catalytic cracking capacity at refineries in Texas is 1,702,317 barrels per calendar day.

Alkylation unit

Alkylation units combine olefins with isoparaffins to form higher octane alkylate that is blended into gasoline. The primary feedstocks for alkylation units are isobutene, C3 olefin, and C4 olefins. Alkylate contains virtually no sulfur or aromatics.

According to Koottungal (2013), 42% of alkylation capacity at refineries in Texas is based on sulfuric acid and the remainder is based on hydrofluoric acid. The total alkylation capacity at refineries in Texas is 333,409 barrels per calendar day.

Hydrotreater unit

Hydrotreaters are used to remove impurities and saturate hydrocarbons. They are used to treat residual streams before routing them to other upgrading processes like reforming. Hydrotreaters whose main purpose is to remove sulfur are sometimes called desulfurization units. Hydrotreaters operated at high pressures, temperatures, and hydrogen concentrations crack as well as treat.

According to Koottungal (2013), 25% of catalytic hydrotreating at refineries in Texas is conducted to pretreat streams fed to catalytic reformers, 6% to conduct other naphtha desulfurization, 10% to desulfurize kerosine/jet fuel, 18% to desulfurize diesel, 7% to treat distillates other than for aromatics saturation, 18% to pretreat streams fed to catalytic crackers, 1% to treat heavy gas oil streams for other reasons, 4% to treat residual streams, 1% for lube oil polishing, 9% for hydrotreating of FCC naphtha, and 1% other. The total catalytic hydrotreating capacity at refineries in Texas is 4,622,115 barrels per calendar day.

Hydrocracker unit

The primary feeds for hydrocrackers are heavy straight run distillate and FCC slurry (residuum). Hydrocracked streams are nearly free of sulfur and are low in aromatics content. Hydrocrackers produce light gases, petrochemical feedstocks, and gasoline and diesel blendstocks.

Many refinery streams can be hydrocracked. From Gary et al (2007):

TABLE 7.1
Typical Hydrocracker Feedstocks

Feed	Products
Kerosine	Naphtha
Straight-run diesel	Naphtha or jet fuel
Atmospheric gas oil	Naphtha, jet fuel, or diesel
Vacuum gas oil	Naphtha, jet fuel, diesel, lube oil
FCC LCO	Naphtha
FCC HCO	Naphtha or distillates
Coker LCGO	Naphtha or distillates
Coker HCGO	Naphtha or distillates

Source: Reference 3 and Reference 6.

LCO and HCO and light and heavy cycle oil, respectively, and LCGO and HCGO are light and heavy cycle gas oil, respectively. The residue from hydrocracking can be blended into heavy fuel oil (US EPA 2004).

According to Koottungal (2013), 66% of catalytic hydrocracking at refineries in Texas is conducted to upgrade distillate streams, 20% to upgrade residuals, 4% to manufacture lube oils, and 10% for other reasons. The total catalytic hydrocracking capacity at refineries in Texas is 457,700 barrels per calendar day.

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Refineries in Texas

Data from US EPA's information collection request to refineries

On April 1, 2011, the US EPA sent an information collection request to refineries in the U.S. The information collection request had three components that were sent to all refineries: (1) a questionnaire on processes and controls; (2) an emissions inventory to be developed using the emissions estimation protocol developed for this effort (US EPA 2011a); and (3) distillation feed sampling and analysis. A fourth component regarding emissions source testing was sent to specific petroleum refineries. The information submitted by refineries is publicly available (except for information identified by refineries as confidential business information) (US EPA not dated). The first and second components are of particular interest for this report; the first component has information about storage tanks at refineries in Texas as well as catalytic crackers, catalytic reformers, and cokers, and the second component has estimated emissions (sometimes for specific compounds) for storage tanks.

The data of interest for this study were extracted from the publicly accessible databases and are contained in supplementary Excel workbook files. Refineries are identified by number.

It was discovered that corrections to information collection request information sent to the US EPA by refineries were not necessarily made to the files identified in the "Sources of information" section. This discovery was made by spot-checking the corrections for refinery #9a (US EPA 2014b). Incorporating those corrections in the information collection request files would be a time-consuming task. No attempt was made to assess the impact, if any, those corrections might make on the results presented in this report.

Supplementary Excel workbook: component 1 intermediate storage tanks Texas with corrected tank ids with STARS heat info sanitized.xlsx

This file contains a list of intermediate storage tanks at refineries in Texas, along with the type of tank, the dimensions of the tank, the throughput in 2009, the average storage temperature, the vapor pressure at the average storage temperature, the type of liquid stored, the type of control exercised when the tank was last degassed, the type of primary and secondary rim seals, the minimum height of the roof for floating roof tanks, the number of times the roof was landed, and the number of times the tank was emptied after the roof was landed. Storage tanks with less than 10,000 gal capacity or that store a liquid with a maximum true vapor pressure less than or equal to 0.1 psi were excluded from the information collection request (US EPA 2011b). Note that according to Trumbore (1999), many asphalts have vapor pressures below 0.1 psi unless the temperature is quite elevated. The entries in this workbook were drawn from a file that had all storage tanks (including crude, wastewater, product, etc. tanks). The intermediate streams of interest for this report were associated with the type of liquid stored in order to create the workbook, and some interpretation was involved in determining which streams are intermediate streams. Notes regarding the sorting process are included in the worksheets titled "Texas storage streams of interest" and "storage tank liquid types." A total of 703 intermediate storage tanks at 26 refineries are listed. Refinery #3 did not disclose any information about tank

contents in this section of component 1 reporting; they only listed their tank ID numbers. This means that it was impossible to tell which of their tanks might be holding intermediates and the data on emissions could not be tied to tank contents for this refinery.

Supplementary Excel workbook: component 2 emissions from intermediate tanks in Texas refinery 16b tank ids corrected sanitized.xlsx

This file contains data on air emissions from storage tanks at refineries in Texas that was submitted in response to the EPA's refinery information collection request. In some cases, the emissions are estimated for individual compounds; in others the emissions are estimated for a group of compounds. Comprehensive speciation of the emissions was not required; the emissions estimation protocol (EPA 2011a) says that refineries should develop emission estimates from storage tanks for the following substances

- Volatile organic compounds (VOC)

Volatile organic hazardous air pollutants (HAPS):

- Benzene
- 1,3-Butadiene
- Cumene
- Diethanolamine
- Ethylbenzene
- n-Hexane
- Methyl isobutyl ketone
- Styrene
- Toluene
- Triethylamine
- 2,2,4-Trimethylpentane
- o-Xylene
- m-Xylene
- p-Xylene
- Xylenes (total)

Semi-volatile and non-volatile organic HAPS (except dioxins, furans, and polychlorinated biphenyls)

- m-Cresol
- o-Cresol
- p-Cresol
- Cresols (total)
- Naphthalene
- Phenol

The protocol says that refineries may develop emission estimates of a number of other compounds depending on available data. Emissions are in short tons per year for the 2010 calendar year. The pollutant description and hazardous air pollutant (HAP) category name are given (if applicable). As with the “component 1 storage tanks Texas.xlsx” workbook, the data presented by the US EPA had data for all storage tanks. This file includes only the tanks listed in the “component 1 storage tanks Texas.xlsx” workbook and there are columns of notes for effecting that sort.

Matching the tank IDs in the estimated emission file with the tank IDs in the tank list resulted in estimated emission data for only 434 storage tanks at 25 of the refineries in Texas. It is plausible that not all of the tanks listed in the component 1 tank list would be present in the component 2 estimated emissions file because some of the estimated emissions might be scrubbed from the files accessible to the public because the refineries designated their emissions as confidential business information. Refinery #3 is missing from the component 2 emissions file because it did not report any non-confidential stream types in its component 1 storage tank element (i.e., all of the fields are blank except for tank ID for this refinery), so it is impossible to tell which of its emissions can be attributed to storage tanks holding intermediates. Refinery #xxx does not appear in the component 2 emissions file.

Close inspection of data revealed that the tank IDs in the list of process equipment from component 1 of the information collection request are slightly different from the tank IDs in the emission inventory for some of the refineries. Except for refinery #16b, if the discrepancies in tank IDs were clear and consistent, the tank IDs in the component 1 file were changed so that they could be linked to the “component 2 emissions from intermediate tanks in Texas refinery 16b tank ids corrected sanitized.xlsx” file, as follows:

- Tank IDs begin with TKTKF in one file and TKFTK in the other for refinery #6 and refinery #13 (example: tank “TKTKF0154” in the component 2 file is “TKFTK0154” in the component 1 file)
- Tank IDs are prefaced with “TANK “ in one file and not the other for refinery #21 (example: tank “S-313” in the component 2 file is “Tank S-313” in the component 1 file)
- Tank IDs are prefaced with “TANK “ in one file and “S-“ in the other for refinery #19 (example: tank “S-195” in the component 2 file is “Tank 195” in the component 1 file)
- Tank IDs were followed by a few spaces and another string of numbers in one file and not the other for refinery #4b (example: tank “91-T4003 874” in the component 2 file is “91-T4003” in the component 1 file)
- Tank IDs were preceded by a number and a dash, then duplicated in one file and not the other for refinery #4a; for this refinery, leading zeros in the tank ID were omitted in one file and not the other (example: tank “572-T13A 572-T13A” in the component 2 file is “T0013A” in the component 1 file)
- Tank IDs had an underscore mark in one file and a hashtag in the other for refinery #8 (for example: tank “49TEF_0718” in the component 2 file is “49TEF#0718” in the component 1 file; this refinery had an unusually high number of tanks listed in the component 1 file that did not appear in the component 2 file, with only 12 of 27 tanks having a tank ID that seemed to match)

- Tank IDs were preceded by entirely different numbers in one file than in the other for refinery #5 (for example, tank “68-95-99A” in the component 2 file is “26-99A” in the component 1 file; this refinery had an unusually high number of tanks listed in the component 1 file that did not appear in the component 2 file also, with only 20 of 44 tanks having a tank ID that seemed to match)
- Tank IDs were preceded by “T-” in one file and not in the other for refinery #18 (for example, tank “896” in the component 2 file is “T-896” in the component 1 file; only 3 of 8 tanks had a tank ID in the component 2 file that seemed to match a tank ID in the component 1 file)
- Tank IDs were preceded by “TK-” in one file and not in the other for refinery #16b (for example, tank “TK-110” in the component 2 file is “T-110” in the component 1 file; only 5 of 14 tanks had a tank ID in the component 2 file that seemed to match a tank ID in the component 1 file)
- Tank IDs were hyphenated in one file and not in the other for refinery #1 (for example, tank “T-215” in the component 2 file is “T215” in the component 1 file).

At refinery #16b, the values in a different column of the component 2 spreadsheet matched the tank IDs in the component 1 spreadsheet, and those values were copied into the regular column of the component 2 spreadsheet.

It was noted that even after correcting as many tank IDs as possible, none of the 27 tanks identified in the component 1 storage tank file as holding propylene were found in the component 2 storage tank emissions file. Propylene is not an intermediate stream and is not of interest for this study, but this highlights the tank ID differences between component 1 and component 2 data.

Supplementary Excel workbook: component 1 Texas refinery details sanitized.xlsx

This file assigns a broad category of refinery type to each refinery in Texas (topping refinery, hydroskimming refinery, upgrading refinery, or heavy oil/asphalt refinery). It also includes information about individual processes at each of the refineries, divided into 50 process types, with throughput capacity for each process, and it has production capacities for 38 product categories/products at each refinery in Texas. A total of 27 refineries in Texas are listed.

Supplementary Excel workbook: component 1 cat crackers Texas sanitized.xlsx

This file contains information in addition to capacity information for fluid catalytic cracking units, non-fluid catalytic cracking units, and catalytic hydrocracking units. A total of 28 crackers at 23 refineries are listed. In contrast, 38 crackers appear in the “component 1 Texas refinery details sanitized.xlsx” file. This data was not filtered by process unit ID, so the missing units are not missing because of unit ID mismatches as was the case for at least one refinery in the storage tank emissions file. The remaining 10 crackers may have been removed because of confidential business information.

Supplementary Excel workbook: component 1 cat reformers Texas sanitized.xlsx

This file contains information in addition to capacity information for catalytic reforming units. A total of 31 reformers at 24 refineries are listed. In contrast, 35 reformers appear in the “component 1 Texas refinery details sanitized.xlsx” file. This data was not filtered by process unit ID, so the missing units are not missing because of unit ID mismatches as was the case for at least one refinery in the storage tank

emissions file. The remaining four reformers may have been removed because of confidential business information.

Supplementary Excel workbook: component 1 cokers Texas sanitized.xlsx

This file contains information in addition to capacity information for coker units. Additional information includes the feed stream to the cokers (this information is available for only 4 cokers). Information about 19 cokers are included in the file (one refinery lists a coker with the same ID in both delayed and fluid coking). Nineteen coking units also appear in the “component 1 Texas refinery details sanitized.xlsx” file.

Data from the US Energy Information Administration

Supplementary Excel workbook: Texas Gulf coast refinery net production.xlsx

Supplementary Excel workbook: Texas inland refinery net production.xlsx

These two files (US EIA 2014c, d) have production data by year for Texas refineries, aggregated into two regions. Net production in thousand barrels per day of crude oil and petroleum products; liquified petroleum gases; ethane-ethylene; ethane; ethylene; propane and propylene; propane; propylene; normal butane-butylene; normal butane; normal butylene; isobutane-isobutylene; isobutane; isobutylene; finished motor gasoline; reformulated motor gasoline; conventional motor gasoline; conventional motor gasoline with fuel ethanol, production of motor gasoline, finished, conventional, ed55 and lower; other conventional motor gasoline; aviation gasoline; kerosene-type jet fuel; commercial kerosene-type jet fuel; military kerosene-type jet fuel; kerosene; distillate fuel oil; distillate fuel oil, 0 to 15 ppm sulfur; distillate fuel oil, greater than 15 to 500 ppm sulfur; distillate fuel oil, greater than 500 ppm sulfur; residual fuel oil; residual fuel oil, less than 0.31% sulfur; residual fuel oil, 0.31 to 1.00% sulfur; residual fuel oil, greater than 1% sulfur; petrochemical feedstocks; naphtha for petrochemical feedstock use; other oils for petrochemical feedstock use; special naphthas; lubricants; naphthenic lubricants; paraffinic lubricants; waxes; petroleum coke; petroleum coke marketable; petroleum coke catalyst; asphalt and road oil; still gas; miscellaneous petroleum products; miscellaneous petroleum products for fuel use; miscellaneous petroleum products for nonfuel use; and processing gain are included.

Other data

Supplementary Excel workbook: Texas refinery unit capacities 2014.xlsx

This workbook gives charge capacities for many processes including catalytic cracking and hydrocracking charge capacities as of January 1, 2014. The refineries in this workbook are identified by number and by region (inland or Gulf Coast). Data used to create this workbook were taken from Koottungal (2013).

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Methods for estimating emissions from storage tanks

For the US EPA's refinery information collection request (US EPA not dated), refineries were asked to either measure tank emissions directly or model them using the equations in Chapter 7 of AP-42 (US EPA 2006a) or by using the US EPA's TANKS Emissions Estimation Software, Version 4.09D software (US EPA 2006b).

The TANKS software is not supported on operating systems older than Windows XP and is in some circumstances less accurate than application of the equations found in Chapter 7 of the US EPA's AP-42 (Miller, 2011). Also, the software and the US EPA's AP-42 Chapter 7 rely on emission estimation equations developed by the American Petroleum Institute (API), and except for a 2005 document about emissions from floating roof tank landings, these sources reference API material from the late 1980s and early 1990s. The API has since updated some of their equations and methodology. The API's most recent editions of these materials revise the equation for stock vapor density, provide an equation for the average vapor space temperature as a function of average ambient temperature, liquid bulk temperature, insolation, and tank surface solar absorptance, provided an equation for normal operating pressure, adjusted the calculation for vapor space outage and turnover factor to take into account the effect of a liquid heel remaining when the tank is empty, and added an expression for the calculating effective throughput (API 2012a and b). The API has also developed methods for estimating emissions from closed-vent internal floating-roof storage tanks (API, 2008). In the reference information and speciation methodology, a new category of solar absorptance factors has been added, an alternative methodology for calculating storage tank temperatures has been added, and the default properties for no. 6 fuel oil have been revised such that there is a significant increase in estimated true vapor pressure and a new default speciation profile has been added (API 2012c with 2013 addendum). The former default properties for no. 6 fuel oil are now presented as suitable for vacuum residual oil.

API provides no default or typical compositions for intermediate refinery streams, other than for vacuum residual oil.

Perhaps the most serious barrier to using the TANKS software for intermediate streams is that there are no libraries of data for intermediate streams and the options for creating customized streams are limited unless vapor pressures at the average, maximum, and minimum tank temperatures are known or have been calculated, along with the molecular weights of the vapor and liquid in the tank.

Ideally, methods for estimating tank emissions would rely on properties that refineries routinely measure, and speciation and property libraries would be available that could be expected to bear some resemblance to the liquids being modeled.

API (2012c with 2013 addendum) provides methods for speciating air emissions from storage tanks by making use of Raoult's Law, which relates the partial pressure of a component to its saturation vapor pressure and the mole fraction of the component in the liquid. Thus, if the liquid weight fraction of the components to be speciated along with the mixture's vapor pressure, liquid molecular weight, and vapor molecular weight are known, speciation of vapor can be estimated. Note that the vapor

molecular weight of various intermediate streams is not established and can only be found if the mole fractions for all the components of a stock vapor are available (API 2012c with 2013 addendum). Libraries of such mole fraction data are not available for intermediate streams, so determining vapor molecular weight requires analysis of vapor samples.

Another means of speciating emissions from storage tanks is to apply a vapor profile for the stream at the storage temperature. The vapor profiles of intermediate streams have not been established at any temperature.

For volatile organic compound emissions from tanks storing asphalt, Deygout (2010) determined that the standing losses from fixed-roof tanks holding hot asphalt would be similar to the losses from fixed-roof tanks that were steam blanked. He found that US EPA's AP-42's method underestimated emissions for straight-run asphalt and visbreaker-cracked residue, while the API methodology slightly overestimated emissions from tanks storing these types of asphalt. Both the US EPA's AP-42 and API methods overestimated the emissions of volatile organic compounds from tanks storing oxidized asphalt. (Deygout relied on the 2002 version of API's Chapter 19 for his formulas). As mentioned in the section on asphalt, Deygout (2010) did not find that emission rates depended on storage temperature for the range of temperatures from 130 to 190°C, but the API and US EPA's AP-42 methods provide results that are temperature dependent. The factors that Deygout found important to emissions from storage tanks holding asphalt (freshness, extent of mixing, and type of asphalt being held) are not considered in the API or US EPA's AP-42 methods. Deygout's findings for asphalt may apply to heated storage tanks holding other highly viscous refinery streams.

Two studies done in Texas compared storage tank emission estimates based on US EPA's AP-42 methodologies to measured emissions (TCEQ 2010; Raun and Hoyt 2011). Both studies used differential absorption light detection and ranging (DIAL) technology to measure emissions.

In Raun and Hoyt (2011), the 95th upper confidence limits of the mean emissions by process area estimated from the DIAL emission measurements using US EPA's ProUCL software were compared to the emission rates estimated from the US EPA's AP-42 formulas. If the true emissions are at the 95% upper confidence limit and not at the mean of the measured results, the true emissions from storage tanks may be underestimated by a factor of as much as 132 for VOCs (from tanks AP-17 and AP-16) and 93 for benzene (from tanks D-350, D-351, D-381, and D-352). It is confusing that the 95% upper confidence limits presented in table 4.4a of that report are equal to or below the means reported in table 3.1 for tanks AP-17 and AP-16. Also, it would have perhaps been more appropriate to compare the 95% confidence interval from the DIAL-measured emissions to the US EPA's AP-42 emission estimates rather than compare the 95% upper confidence limit from the DIAL-measured emission to the US EPA's AP-42 emission estimates. The information presented by Raun and Hoyt (2011) is insufficient to determine what the 95% confidence intervals of the DIAL measurements were. In addition, tank data used to produce the AP-42 estimates of this study were received in a personal communication (Hansen 2014) and casual inspection raises potential concerns about the quality of that data. For example, the reported molecular weight of the vapor is in some cases higher than the molecular weight of the liquid in the tank, and in some cases the molecular weight of the vapor over a liquid mixture is not lower than

the molecular weight of the liquid. In some cases, tank temperatures appear unreasonably low. The effect, if any, that this would have had on the AP-42-based estimates of emissions is unknown. More analysis is needed to verify Raun and Hoyt's (2011) conclusions about inaccuracies in the AP-42 estimation methods.

In TCEQ (2010), measured results (using DIAL) were sometimes higher than emissions estimated using the US EPA's AP-42 methodologies and sometimes lower. For example, 9 out of 10 measured values from one set of scans were below the US EPA's AP-42-based estimate (which was dominated by one of four tanks included as a potential input to the measured values), but 4 out of 4 measured values from another set of scans that included most of the same tanks were above the US EPA's AP-42-based estimates.

Tank temperatures

Tank temperature influences vapor pressure and is a very important factor in the AP-42-based emission estimates. Tanks storing very heavy streams are generally maintained at a high enough temperature to keep the material in the tank at a low enough viscosity to be pumped. In the refinery information collection request data (EPA not dated), some of the tank temperatures for residuum appear to be near ambient. Refinery #12, for instance, reports ten storage tanks holding "Unfinished oils – Residuum" whose temperatures range from 75 to 86°F. It could be that these tanks were not holding material that fits the US EIA (not dated) definition of residuum ("residue from crude oil after distilling off all but the heaviest components, with a boiling range greater than 1000°F"), or that the residuum in these tanks was under long-term storage and was not heated, or that the reported temperatures are inaccurate.

The minimum short-term storage tank temperature for a tank holding residuum or asphalt can be calculated by applying the correlation for predicting viscosity of heavy oils and asphalt at various temperatures given in the introduction to this report. The rule of thumb is that the minimum tank temperature is the temperature at which viscosity is 2 Pa·s (Błażejowski et al 2014). To avoid iteration one can find the viscosity at 30°C, then find the constants B and s as follows:

$$B = \log(\mu_{30^{\circ}\text{C}}) + 3.0020$$
$$s = 0.0066940\log(\mu_{30^{\circ}\text{C}}) + 3.5565$$

Next, the equation for t at a viscosity of 2 Pa·s can be solved to get

$$t_{\text{minimum}} = \frac{303.15}{\left[\frac{\log(2 \text{ Pa}\cdot\text{s}) + 3.0020}{B} \right]^{1/s}} - 273.15$$

If the viscosity at 30°C is not given, it can be found from the viscosity at a temperature other than 30°C by using the BASIC code given in the section on the correlation for predicting viscosity of heavy oils and asphalt at various temperatures given in the introduction to this report. If the viscosities at temperatures bracketing 30°C are given, an estimate of the viscosity at 30°C can be made by fitting the data points to a power function. Two vacuum gas oils produced minimum storage temperatures well

below the pour point using these correlations, which indicates that the heavy oils these correlations are intended for might not include heavy gas oils.

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Cutter stock

Information about cutter stock added to streams and stored in tanks prior to downstream processing steps was sought for this report. Sometimes cutter stock is blended into heavy streams prior to processing in an FCCU in order to reduce coking; if the cut stream was stored in a tank prior to being fed to the FCCU, information about its cutter stock would need to be known in order to understand emissions from that storage tank.

Cutter stock frequently refers to material blended into streams in order to meet product specifications for viscosity. This blending does not occur until after downstream processing, if any, has occurred. In some cases, downstream processing is conducted partly because it reduces the need for cutter stock (cutter stock is usually of higher value than the heavy streams it is blended with). While tanks holding product streams are not the subject of this report, the following quote about cutter stock in product streams provides useful context about some of the difficulties of pinning down the properties of cutter stock (US EPA 2004):

The Heavy Fuel Oils (HFOs) category includes both finished products (residual fuels) and the primary refinery streams from which they are blended.... The finished heavy fuels (residual fuels) are products that consist primarily of the residuum of the refining process after virtually all of the higher-quality hydrocarbons have been distilled, cracked, or catalytically removed from crude oil feedstock. To produce a residual fuel of a specified viscosity, the high viscosity of the residual streams is reduced by adding a diluent (cutter stock) that is typically a lower quality distillate stream. The choice of the distillate cutter stock is itself variable and largely a function of availability at any given time within the refinery and the viscosity specifications of the product being manufactured. For instance, in refineries with catalytic cracking units, catalytically cracked cycle oils are common fuel diluents (CONCAWE, 1998). Because residual fuels are blended from a variety of different residual and distillate materials, the specifications for residual fuel oils are very general, with viscosity being the controlling specification. The exact blend used for a specific residual fuel is determined largely by the desired viscosity of the finished fuel and specifications set by ASTM (2002). As a result, the composition of residual fuel oils can vary widely and will depend on the refinery configuration, the crude oils being processed and the overall refinery demand.

Note that this paragraph is referring to variability in cutter stock for residual fuels only, not all potential cutter stock streams at refineries. US EPA (2004) goes on to say that low-viscosity, low-polycyclic aromatic compound streams are sometimes used as cutter stock in specialty products like cutback asphalt.

An MSDS for refinery #10 (Refinery #10 2006d) reveals that a synonym for light cycle oil (presumably from the FCCU) is "middle distillate cutter oil."

If a tank is holding fuel oil at a known temperature, a rough idea of the minimum fraction of cutter stock it contains can be made by assuming a residual oil base and a cutter stock with known viscosities. The viscosities at the actual tank temperature can be estimated using the correlations presented in the intermediate streams section of this report, and the methods described by Stratiev and others (2008) can be used to iterate until the fraction of cutter stock at a combined viscosity of 2 Pa-s (the minimum

pumping viscosity) is found. Note that dynamic viscosity (given in units of centistoke, for example) can be converted to kinematic viscosity (given in units of Pascal-seconds) if the density of the fluid is known.

API (2012 with 2013 addendum) says that if no specific information is given about the ingredients of fuel oil no. 6, then vapor pressure can be estimated by applying Clausius-Clapeyron equations constants of 10.781 for A and 8933°R for B. These equation constants were developed by assuming a mixture of vacuum residual oil with 20% kerosene or 25% diesel as the cutter stock.

This table gives the vapor pressure for four cutter stocks across a range of temperatures (API 2012c with 2013 addendum):

Temp °F	Sample ID			
	Vapor pressure, Torr			
	A2	B2	C2	D2
32	0.47	0.94	0.13	0.27
68	1.5	2.1	0.45	0.74
100	3.7	3.8	1.15	1.6
150	13.5	8.6	4.5	5
200	37	17	13.5	12
250	90	31	35	26
300	205	52	80	52
350	410	88	170	96
400	480		330	165
450	760		580	
480			760	

The vapor pressures in this table were measured using an isoteniscope. The vapor pressures of these streams measured using the HOST method at 100°F are 0.006, 0.014, 0.006, and 0.060 psia for stream A2, B2, C2, and D2, respectively. The API gravities of streams A2, B2, C2, and D2 are 16.4, 5.2, 6.3, and 20.6, respectively.

The concentrations of organic compounds in ppmw in the four cutter stock samples of the previous table are given below (API 2012 with 2013 addendum):

Compound	Type of analyte	Cutter stock sample ID			
		A2	B2	C2	D2
Biphenyl	PAH	225	118	2170	113
Naphthalene	PAH	1120	1050	5250	1000
Phenanthrene	PAH	8.1	1440	4360	1380
Fluoranthene	PAH	0.132	103	113	94.4
Benz[a]anthracene	PAH		188	25.8	180
Chrysene	PAH	0.145	296	46.4	284
Benzo[b]fluoranthene	PAH		36.1		35.3
Benzo[k]fluoranthene	PAH		17.8		18.4
Benzo[a]fluoranthene	PAH		7.21		5.84
Benzo[a]pyrene	PAH		127	3.5	122
Indeno[1,2,3-cd]pyrene	PAH		13.6		15.4
Dibenz[a,h]anthracene	PAH		18.1		18.5
Benzo[g,h,i]perylene	PAH		53.5		50.5
Hexane	PIANO high	71.9	40.6	35.7	37.2
Cyclohexane	PIANO high	78.5	12.9	33.2	11.8
Benzene	PIANO high	26.2	28.4	40.4	26.9
Isooctane	PIANO high				
Toluene	PIANO high	682	268	523	260
Ethylbenzene	PIANO high	846	133	348	131
p/m-Xylene	PIANO high	3000	607	1470	598
Styrene	PIANO high		2.97		2.91
o-Xylene	PIANO high	1570	268	691	263
Isopropylbenzene	PIANO high	337	9.81	27.7	9.71
1,2,4-Trimethylbenzene	PIANO high	5940	813	2250	810
Naphthalene	PIANO high	1770	1280	3330	1320
Phenol	Phenol	5.02	4.69	1.75	4.75
2-Methylphenol	Phenol		10.8		11.1
3,4-Methylphenol	Phenol		14.8	3.75	15.3
Benzo(j)fluoranthene	Heavy PAH				
Dibenzo(a,i)pyrene	Heavy PAH		9.6		9.12
Dibenzo(a,e)pyrene	Heavy PAH		2.8		2.96
Dibenzo(a,h)pyrene	Heavy PAH				2.01

Notes: PIANO=paraffins, isoparaffins, aromatics, naphthenes

Literature

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Summary

Data from the US EPA's refinery information collection request contains detailed information about storage of intermediates at refineries in Texas. In some cases, pieces are missing because the information was not requested or because it was designated by the submitting refinery as confidential business information. In these cases, data from other sources is sometimes available.

Refineries vary a great deal in their configurations and in the crude oil they process, not just from refinery to refinery but from time to time within the same refinery. Because of this, it is difficult to generalize about the fate and qualities of intermediate streams, or about the profile of their vapor emissions. For example, there is no value for vapor pressure that could generally be applied to all light gas oil streams or to the constants that can be used to determine the vapor pressure of light gas oil at different temperatures. There is also no set of correct values for vapor speciation for light gas oil. The best that can be done is to determine from available data what the range of properties and vapor speciation might be.

Using available data is complicated by the non-uniformity of the language used for streams at refineries. A term that is applied to a stream at one refinery might apply to a different stream at another refinery. The same streams at different refineries may be given different names. An example of the looseness of the language used is demonstrated at refinery #14 where a liquid stock described as "kerosene" was assigned a higher molecular weight than a liquid stock described as "gas oil." (The molecular weights in this case may or may not be in error, even though gas oils usually refer to streams heavier than kerosene; since there is no agreed-upon standard, streams can be named arbitrarily.) The usefulness of libraries of intermediate stream data would be improved by uniformity in language.

Identifying intermediate liquids at least loosely on the basis of properties might facilitate a systematic assessment of emissions from intermediate storage tanks. Emissions are influenced by stream volatility and volatility can be related to a number of properties that might be commonly assessed by refineries. Also, speciation of emissions would be expected to be influenced by whether the stream has undergone a cracking process (cracked streams tend to contain more aromatics than straight-run streams). One example of a potentially useful means of categorizing intermediate streams, assuming that refineries generally know the boiling point ranges of these streams, might be

- Straight-run naphtha (122-400°F)
- Straight-run light gas oil (401-650°F)
- Straight-run heavy gas oil (651-1000°F)
- Straight-run residuum (1000°F+)
- Cracked naphtha (122-400°F)
- Cracked light gas oil (401-650°F)
- Cracked heavy gas oil (651-1000°F)
- Cracked residuum (1000°F+)

Intermediate streams are understood to be unfinished; in other words, they are not final product nor are they in general intended for blending into final product. Actual streams at refineries might not necessarily fit neatly into any property-based category scheme, but if they were identified as belonging to the category they most resembled or perhaps a mix of categories, it would be an improvement over relying on common names given to intermediate streams.

Unlike many of US EPA's emission estimation methodologies, the US EPA's storage tank emission estimation methods are largely based on fundamental principles and not on throughput-based factors that were determined from measured emissions. Insufficient work has been done to know for sure whether AP-42 emission estimation methodologies for tanks holding intermediates at refineries are accurate. It appears that for certain storage scenarios (such as fresh stirred asphalt or loading of light streams), the equations may not capture the most important emission mechanisms, or may fail to capture important factors such as non-uniform vapor composition in tank head space. It may be that a combination of the fundamental principle equations, with throughput-based emission factors when particular scenarios are occurring, would provide more accurate estimates of emissions from storage tanks. In addition, the US EPA's AP-42 equations could be reviewed to determine if there are elements that require undue effort, considering the broad uncertainties involved in other elements.

Even were the US EPA's storage tank emission methods to capture the important emission mechanisms, the libraries of information available for determining the physical properties of intermediate streams and the composition of their liquids and vapors are exceedingly poor.

A study designed to produce statistically meaningful measured emission estimates from tanks holding intermediates under different conditions (i.e., while loading, unloading, static; with fresh and aged contents in the case of asphalts and residues) along with careful documentation of tank characteristics (including mixing energy, any heating methods, and any blanketing) and stream properties used to produce corresponding AP-42 emission estimates, would be a useful first step towards understanding the relationship between AP-42 emission estimates and actual storage tank emissions. Existing comparisons of measured and AP-42 estimated results do not conclusively prove that AP-42 emission estimates are inadequate, let alone whether they produce low results because they neglect important emission mechanisms or because the composition and physical properties of intermediate streams are poorly understood.

Further synthesis of the raw data gathered during this effort is needed in order to better understand the practicalities of applying the EPA's AP-42 estimation methodologies to storage tanks holding intermediates at refineries. This would include assigning streams to property-based categories to determine if any categorization scheme would result in a range of values narrow enough to be useful, along with calculation of variables such as slopes at 10 vol % evaporation and the Clausius-Clapeyron vapor pressure equation constants, where possible. Also, the relationships AP-42 provides for estimating properties such as vapor pressure at different temperatures need to be tested by comparing to measured values for intermediate refinery streams.

Future work might also include building on the worksheets of stream composition and property data created for this project. In particular, there are a number of crude oil assays that could be included in the library (see, for example, Professor Jechura's Petroleum Refining Processes class notes page at inside.mines.edu/~jjechura/Refining).

Appendix A: Crude assays

Assays of crude oils fed to Texas refineries

HOOPS Blend crude is delivered mainly into Texas City, TX (ExxonMobil Refining and Supply not dated a). Assay data (ExxonMobil Refining and supply not dated c) contain information on distillation cuts including initial and final boiling point, pour point, viscosity at various temperatures, naphthalenes (kerosene cut only), a distillation summary for each distillation cut, and hydrocarbon types found in each distillation cut. See:

Supplementary Excel workbook: HOOPS Blend assay by ExxonMobil.xls

Thunder Horse crude is transported to refineries in Louisiana, Texas, the mid-continent and the Midwest (ExxonMobil Refining and supply not dated b). Assay data (ExxonMobil Refining and Supply not dated d) contain information on distillation cuts including initial and final boiling point, pour point, viscosity at various temperatures, naphthalenes (kerosene cut only), a distillation summary for each distillation cut, and hydrocarbon types found in each distillation cut. See:

Supplementary Excel workbook: Thunder Horse assay by ExxonMobil.xls

Hibernia assay

Hibernia crude is not typically sold to Gulf Coast refineries. An assay of Hibernia crude by Chevron includes the values found in the ExxonMobil assays (except for naphthalenes) (Chevron 2011). See:

Supplementary Excel workbook: Hibernia assay by Chevron.xls

Santos assays

Crudes assayed by Santos (not dated a, b, c, d, e) would not be expected to be fed to Texas refineries but might bear some resemblance to some of the Nigerian and Angolan crudes historically imported by Texas Gulf Coast refineries (this importation has dropped off recently in favor of domestic crudes). Cooper Basin, Kutubu, and Mutineer Exeter crudes all have very high API gravity (mid 40's) and very low sulfur (.03-.04% by mass), values that are similar to Agbami crude from Nigeria. Crude from Stag has very low API gravity (18.5°), similar to crude from the Kuito basin in Angola, but with a fraction of the sulfur (0.14% by mass). Barrow Island crude is in the middle, with an API gravity of 36.1° and a sulfur content of 0.05% by mass. It most resembles Pennington crude from Nigeria. The Santos assays contain some information about distillation cuts (molecular weights, vapor pressure, compound speciation) that the assays of crudes fed to Texas refineries do not.

Cooper Basin crude oil summary of major cuts (Santos not dated a):

Cooper Basin crude oil
- Summary of Major Cuts

	Whole crude	Naphtha			Kerosene	
		70 - 140	140 - 165	165 - 190	140 - 230	190 - 230
Boiling Range [C		70 - 140	140 - 165	165 - 190	140 - 230	190 - 230
Boiling Range [F		158 - 284	284 - 329	329 - 374	284 - 446	374 - 446
Yield Range vol%		5.8 - 14.7	14.7 - 18.6	18.6 - 24.4	14.7 - 36.4	24.4 - 36.4
Yield Range wgt%		4.6 - 12.7	12.7 - 16.5	16.5 - 22.2	12.7 - 34.0	22.2 - 34.0
Yield vol%		8.9	3.9	5.8	21.7	12
Yield wgt%		8.1	3.8	5.7	21.3	11.8
API Gravity [API	44.6	59.9	53.3	52	50.7	49.1
Specific Gravity 60/60 [F	0.8034	0.7392	0.7657	0.7711	0.7768	0.7835
Density 15[C g/ml	0.803	0.7389	0.7654	0.7708	0.7765	0.7832
Mercaptan Sulphur ppm	<1					
Total Sulphur wgt %	0.02					
Total Sulphur ppm		40	48	31	31	22
Reid Vapour Pressure psi	2.3					
Reid Vapour Pressure kpa	15.75					
Basic Nitrogen ppm	31					
Total Nitrogen ppm	73					
Total Nitrogen wgt%						
Sediment wgt%	<0.01					
Water Content v/v%	<0.025					
n-Paraffins vol%		30	33.8	42		
iso-Paraffins vol%		26.9	28.5	22		
Naphthenes vol%		33.5	22.7	23		
Aromatics (FIA) vol%		9.6	15	13		
Freezing Point [C			13.6	12	11.6	10.6
Cloud Point [C				-59	-49.5	-39
Pour Point [C	9					
Flash Point (Abel) [C	-4.5			43	44.5	
Smoke Point mm				33	32	33
Aniline Point [C					65.3	70.1
Cetane Index						51.9
Wax Content wgt%	7.4					
Softening Point of Wax [C	33 - 39					
Viscosity @ 20[C cSt	3.598					
Viscosity @ 40[C cSt	2.396			0.959	1.112	1.34
Viscosity @ 50[C cSt						
Viscosity @ 70[C cSt						
Viscosity @ 100[C cSt						
Total Acid Number mg KOH/g	0.05					
Conradson Carbon Residue wgt%	0.24					
UOP K Factor	12.4					
Salt Content lb/1000 bbls	<1					
Salt Content w/w ppm	<4					
Heat of Combustion (gross) MJ/kg	46.24					
Heat of Combustion (nett) MJ/kg	43.29					
Asphaltenes wgt%	0.1					
Ash Content wgt%	<0.01					
Nickel ppm	< 0.5					
Vanadium ppm	< 0.5					
Copper ppm	<1					
Sodium ppm	4					
Iron ppm	2					

- Refinery Intermediate Product Literature Review Project: Final Report -

Cooper Basin crude oil
- Summary of Major Cuts

	Gas Oils		Vacuum Gas Oil	Residues	
Boiling Range [C	230 - 330	230 - 360	360 - 540	360+	540+
Boiling Range [F	446 - 626	446 - 680	680 - 1004	680+	1004+
Yield Range vol%	36.4 - 67.2	36.4 - 75.7	75.7 - 98.7	75.7 - 100.0	98.7 - 100
Yield Range wgt%	34.0 - 65.3	34.0 - 74.1	74.1 - 98.4	74.1 - 100.0	98.4 - 100
Yield vol%	30.8	39.3	23	24.3	1.3
Yield wgt%	31.3	40.1	24.3	25.9	1.6
API Gravity [API	41.6	41.2	35.2	33.6	14.3
Specific Gravity 60/60 [F	0.8176	0.8193	0.8488	0.8571	0.9706
Density 15[C g/ml	0.8172	0.8189	0.8484	0.8567	0.9701
Mercaptan Sulphur ppm					
Total Sulphur wgt %	0.02	0.02	0.08	0.09	0.24
Total Sulphur ppm					
Reid Vapour Pressure psi					
Reid Vapour Pressure kpa					
Basic Nitrogen ppm					
Total Nitrogen ppm			151	233	
Total Nitrogen wgt%					0.2
Sediment wgt%					
Water Content v/v%					
n-Paraffins vol%					
iso-Paraffins vol%					
Naphthenes vol%					
Aromatics (FIA) vol%					
Freezing Point [C					
Cloud Point [C	-9	5			
Pour Point [C	-12	3	36	36	39
Flash Point (Abel) [C					
Smoke Point mm					
Aniline Point [C		82	103.9	107.4	
Cetane Index		60.2			
Wax Content wgt%		0.1	35.3	29.9	
Softening Point of Wax [C					
Viscosity @ 20[C cSt					
Viscosity @ 40[C cSt		3.14			
Viscosity @ 50[C cSt			10.47	13.45	
Viscosity @ 70[C cSt		1.914			1700
Viscosity @ 100[C cSt			3.506	4.15	203.4
Total Acid Number mg KOH/g					
Conradson Carbon Residue wgt%			0.04	1.1	
UOP K Factor					
Salt Content lb/1000 bbls					
Salt Content w/w ppm					
Heat of Combustion (gross) MJ/kg					
Heat of Combustion (nett) MJ/kg					
Asphaltenes wgt%				0.55	
Ash Content wgt%					
Nickel ppm				0.5	12.5
Vanadium ppm				<0.5	1
Copper ppm					
Sodium ppm					
Iron ppm					

Kutubu crude oil summary of major cuts (Santos not dated b):

Kutubu crude oil - Summary of Major Cuts

	Whole crude	light naphtha	medium naphtha	wide cut kero	Atmos. Gas oil	Atmos. Residual
TBP Temp at Start °C	Start	18	70	140	230	360
TBP Temp at End °C	End	70	140	230	360	End
TBP Temp at Start °F	Start	64	158	284	446	680
TBP Temp at End °F	End	158	284	446	680	End
Yield at Start vol%		4.5	14	37.2	55.7	79.3
Yield at End vol%		14	37.2	55.7	79.3	100
		9.5	23.2	18.5	23.6	20.7
Gravity API	44.8					23.2
Density @ 15°C	0.803	0.653	0.743	0.798	0.858	0.914
Sulphur ppm	460	5	5	20	380	1450
Mercaptan Sulphur ppm			<3	<3		
Nitrogen ppm	350				62	1510
P/N/A vol%		90/9/1	42/49/9			
Research Octane Number		75.5				
FIA Aromatics vol%				21		
Napthalenes vol%				1.6		
Viscosity @ 20°C cSt	2.36					
Viscosity @ 40°C cSt					3.26	
Viscosity @ 50°C cSt						34.7
Freeze Point °C				-55		
Freeze Point °F				-67		
Cloud Point °C					-4	
Cloud Point °F					25	
Pour Point °C	-3				-3	42
Pour Point °F	27				27	108
Wax wt%	6.4					
Cetane Index ASTM D4737					49.1	
Smoke Point mm ASTM				23		
Aniline Point °C				50		87.9
Aniline Gravity Product				5580		4420
Ash wt%	0.005					0.02
Asphaltenes wt%	0.04					0.23
Conradson Carbon Residue wt%	0.47					2
Total Acid number mg KOH/g	0.07			0.05	0.06	0.09
Metals Ni/V ppm	1<1					3/<1

Mutineer-Exeter crude oil summary of major cuts (Santos not dated c):

Summary of Major Cuts

	Whole Crude	Naphtha			Kerosene		Distillates		Vacuum Gas Oils	Residues	
Boiling Range °C		18-70	70-140	140-190	140-230	190-230	230-340	230-360	360-510	360+	510+
Boiling Range °F		64-158	158-284	284-374	284-446	374-446	446-644	446-680	680-950	680+	950+
Yield Range vol%		0.11-2.15	2.15-23.19	23.19-40.21	23.19-53.01	40.21-53.01	53.01-81.14	53.01-84.76	84.76-98.71	84.76-100	98.71-100
Yield Range wgt%		0.21-1.93	1.93-20.85	20.85-36.97	20.85-49.67	36.97-49.67	49.67-79.34	49.67-83.27	83.27-98.45	83.27-100	98.45-100
Yield vol%		2.05	21.03	17.03	29.83	12.8	28.13	31.74	13.95	15.24	1.29
Yield wgt%		1.72	18.92	16.12	28.82	12.69	29.68	33.61	15.18	16.73	1.55
API Gravity	43.4	83.9	62.1	53	49.4	44.8	34.2	33.7	29.5	27.8	13.9
Density 15° C g/ml	0.8091	0.6566	0.7305	0.7665	0.7819	0.8023	0.8536	0.8561	0.8784	0.8876	0.9729
Sulphur as Mercaptans ppm	<3	<3	<3	<3	<3						
Total Sulphur wgt %	0.033						0.027	0.035	0.074	0.096	0.269
Total Sulphur ppm		<3	<3	3	13	27					
Total Nitrogen ppm	32							12	62	183	1046
Basic Nitrogen ppm	17								54	80	
Paraffins vol %		97	59	62							
Naphthenes vol%		3	41	32							
Aromatics vol%		0	0.2	3.8							
Unidentified vol%											
Reid Vapour Pressure kPa	9	68.25	12.5								
Reid Vapour Pressure psi	1.3	9.9	1.8								
Total Acid Number mg KOH/g	<0.05				0.011			0.04	0.1	0.13	0.26
Research Octane Number (calc.)		72.5	57.4								
Viscosity -20°C cSt					3.02	4.78					
Viscosity 20°C cSt	3.03				1.44	1.97					
Viscosity 40°C cSt	2.23				1.1	1.43		3.61			
Viscosity 50°C cSt									16.9	21.2	
Viscosity 100°C cSt									4.52	5.65	102.6
Freezing Point °C					<-60	-42					
Smoke Point mm				44	38	30					
Aromatics (FIA) vol%				3.1	6	10.4					
Naphthalenes vol%					0.08	0.2					
Aniline Point °C					64.7			68.4		96.4	
Aniline Point °F					148.5			155.1		205.5	
Aniline Gravity Product					7329			5225		5713	
Flash Point (Abel) °C					40.5						
Cetane Index (D976)								47.6			
Saybolt Colour					30	30					
ASTM colour								10.5			
Copper Corrosion					1b			1b			
Cloud Point °C							-13	-7			
Pour Point °C	12						-12	-6	39	42	60
Micro Carbon Residue wgt%	0.2							<0.1	0.9	13.3	
Gross Heating Value MJ/kg	46.15								44.95		
Nett Heating Value MJ/kg	43.22								42.27		
Wax Content wgt%	3							<1	30.8	27.6	
Ash wgt%	0.004									0.014	0.034
Asphaltenes wgt%	0.03								0.02	0.18	3.6
UOP K Factor	11.9								12.2	12.1	
Saturates (HPLC) wgt%							65.2				
Aromatics (1 ring) HPLC wgt%							17.5				
Aromatics (2 ring) HPLC wgt%							8				
PNA (HPLC) wgt%							9.3				
Carbon Content wgt%	84									87.29	
Hydrogen Content wgt%	13.88									13.81	
Nickel ppm	<1								<1	<1	9
Vanadium ppm	<1								<1	<1	8
Iron ppm	<1								<1	1	8
Sodium ppm	2								<1	10	41
Copper ppm	<1								<1	<1	<1
Mercury ppb	3										

Barrow Island crude oil summary of major cuts (Santos not dated d):

Barrow Island - Summary of Major Cuts

	Whole crude	Light Naphtha	Medium Naphtha	Heavy Naphtha	Kero	Atm Gas Oil	Light VGO	Heavy VGO	Vacuum Resid	Atm Resid
TBP Temp at Start °C		10	80	150	200	260	340	430	570	340
TBP Temp at End °C		80	150	200	260	340	430	570	end	end
TBP Temp at Start °F		55	175	300	400	500	650	800	1050	650
TBP Temp at End °F		175	300	400	500	650	800	1050	end	end
Yield at Start vol%		1.4	7.6	27.2	43.9	61.1	81.3	91.2	98.9	81.3
Yield at End vol%		7.6	27.2	43.9	61.1	81.3	91.2	98.9	100	100
Yield of Cut (wt% of Crude)		5	17.8	15.9	17.7	21.5	10.9	8.8	1.4	21.1
Yield of Cut (vol% of Crude)		6.2	19.6	16.7	17.2	20.2	9.9	7.7	1.1	18.7
Gravity, °API	37.7	79.1	55.3	45.8	33.8	27.8	21.4	15.9	7.7	18.2
Specific Gravity	0.8363	0.6718	0.7577	0.7979	0.8559	0.8885	0.9252	0.9601	1.0164	0.945
Sulphur, wt%	0.05	0.003	0.004	0.007	0.02	0.04	0.1	0.19	0.34	0.15
Mercaptan Sulphur, ppm		9	2	2	2					
Nitrogen, ppm	320					30	280	2600	3800	1500
Hydrogen, wt%		16	14.7	15.1	13.9	13.2	12.4	11.6		
Viscosity @ 40°C (104°F) cST	1.9			1.01	1.9	4.55	26.7	290		
Viscosity @ 50°C (122°F) cST	1.64			0.873	1.56	3.53	17.9	150	3.34E+05	82.5
Viscosity @ 100°C (212°F) cST				0.498	0.752	1.41	4.48	17.6	2160	13.4
Viscosity @ 135°C (275°F) cST							2.43	7.24	350	6.16
Freeze Point, °C				<-70	-60	-31				
Freeze Point, °F				<-90	-76	-23				
Pour Point, °C	-54			<-70	-66	-36	-2	22	56	8
Pour Point, °F	-65			<-90	-86	-33	30	70	135	45
Smoke Point, mm (ASTM)				22	16					
Aniline Point, °C				52	53	54	67	83	90	75
Aniline Point, °F				125	127	130	152	182	194	167
Total Acid Number, mg KOH/g	0.1		0.05	0.06	0.06	0.07	0.08	0.08	0.09	0.08
Cetane Index, ASTM D976				33	35	40				
Diesel Index				57	43	36				
Characterisation Factor (K Factor)	11.7		11.6	11.7	11.3	11.3	11.4	11.5	11.7	11.6
Research Octane Number, Clear		74.9	60.2	41.2						
Motor Octane Number, Clear		71.4	58.4							
Paraffins, vol%		78.1	37.7	45.7	41.6					
Naphthenes, vol%		21.9	58	42	39.5					
Aromatics, vol%		0	4.3	12.3	18.9					
Molecular Weight	168	98	110	142	168	209	285	406	566	328
Gross Heating Value, MM BTU/bbl	5.77	4.89	5.35	5.57	5.85	6.01	6.18	6.34	6.57	6.28
Gross Heating Value, kcal/kg	10970	11550	11210	11080	10860	10730	10590	10480	10250	10530
Gross Heating Value, MJ/kg	45.9	48.3	46.9	46.4	45.5	44.9	44.3	43.9	42.9	44.1
Heptane Asphaltenes, wt%	<.1								1.9	0.1
Micro Carbon Residue, wt%	0.4								29.6	1.9
Ramsbottom Carbon wt%	0.36								27	1.7
Vanadium, ppm	<.1								1	0.1
Nickel, ppm	2								110	7

Stag crude oil summary of major cuts (Santos not dated e):

Stag crude oil - Summary of Major Cuts

	Whole crude	Kerosene	Gas Oil	Vacuum Distillates	Atmospheric Residues	Vacuum Residues
Boiling Range C		IBP - 230	230 - 360	360 - 522	360+	522+
Boiling Range F		IBP - 446	446 - 680	680 - 972	680+	972+
Yield Range vol%		0 - 4.9	4.9 - 52.9	52.9 - 91.4	52.9 - 100	91.4 - 100
Yield Range wt%		0 - 4.4	4.4 - 50.9	50.9 - 90.6	50.9 - 100	90.6 - 100
Yield vol%		4.9	48	38.5	47.1	8.6
Yield wt%		4.4	46.5	39.7	49.1	9.4
API Gravity API	18.3	28.6	22.8	14.6	13	6.2
Specific Gravity 60/60 F	0.9447	0.884	0.9171	0.9684	0.9793	1.0276
Density 15 C kg/l	0.9442	0.8835	0.9166	0.9679	0.9787	1.027
Total Sulphur wt %	0.1	<0.01	0.04	0.16	0.17	0.22
Total Nitrogen wt%	0.073			0.1	0.15	0.39
Basic Nitrogen wt%	0.03			0.04	0.07	
Butane and Lighter vol%	nil					
Aromatics by FIA vol%		3.9				
Aromatics by HPLC wt%			23.1			
Reid Vapour Pressure psi	nil					
Total Acid Number mg KOH/g	0.45		0.07	0.56	0.81	
Kinematic Viscosity -20 C cSt		12.65				
Kinematic Viscosity 20 C cSt	124	3.626				
Kinematic Viscosity 40 C cSt	38.5	2.405	7.285			
Kinematic Viscosity 50 C cSt				136.9	492.7	
Kinematic Viscosity 100 C cSt				12.85	28.2	1093
Freezing Point C		<-80				
Smoke Point mm		16				
Copper Strip Corrosion			1A			
Aniline Point C		52.3	55	60.9	64.4	
Aniline Point F						
Aniline Gravity		3606	2987	2067	1923	
Flash Point (Pensky-Martens) C	110					
Cetane Index (ASTM D 976)			34.4			
Cetane Index (ASTM D 4737)			33.4			
ASTM Colour			L0.5			
ASTM Distillation 10% Point C			274.5			
ASTM Distillation 50% Point C			296			
ASTM Distillation 90% Point C			332			
Cloud Point C			<-48			
Pour Point C	-30		<-48	-6	12	45
Conradson Carbon Residue wt%	1.2				2.6	
Water Content vol%	0.3					
Gross Heating Value MJ/kg	43.8				43.4	
Nett Heating Value MJ/kg	41.3				41	
Wax Content wt%	0.2					
Ash Content wt%	0.05				0.1	
Asphaltenes wt%	0.05				0.05	
Sediment wt%	0.1					
UOP K Factor	11.1				11.2	
Nickel ppm	3				8	38
Vanadium ppm	<1				<1	2

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Santos. Not dated d. Barrow Island - summary of major cuts. Accessed at www.santos.com/library/barrow_crude.pdf on July 4, 2014.

Santos. Not dated e. Stag crude oil - summary of major cuts. Accessed at www.santos.com/library/stag_crude.pdf on July 4, 2014.

Appendix B: PAH concentrations in refinery streams

Average concentrations of PAHs in refinery streams (CPPI 2011)

Table 14-1 Average Concentrations of PAHs in Refinery Streams (from 2001 CPPI Study)

Substance Name	Average Stream Composition (mg/kg)																				
	Crude	Gas	Diesel	HFO	CC Bttm	Lube Dist	Asphalt	AGO	VGO	LCO	HCO	HC Dist	HC GO	HC Bttm	Cat Feed	ATB	TC Res	HP VD	LP VD	Jet	Arom
Acenaphthene	14.8	7.3	77.1	162.3	70.5	0.0	0.0	35.7	14.9	1245.3	217.4	4.6	0.0	0.0	59.8	10.2	0.0	0.0	0.0	29.3	20.9
Acenaphthylene	2.5	0.0	1.9	0.0	3.6	0.0	0.0	2.1	1.6	13.1	2.2	0.0	0.0	0.0	3.4	0.0	0.0	0.0	0.0	0.0	2.6
Anthracene	2.8	9.2	6.0	72.8	122.3	0.0	0.0	11.3	22.5	508.1	740.0	0.0	1.2	0.0	44.7	0.0	3.4	0.0	0.0	5.0	15.1
Benz(a)anthracene	6.4	5.3	2.5	144.9	1098.7	46.3	0.0	7.9	8.3	11.3	344.0	0.0	0.0	0.0	33.5	11.0	0.0	2.6	65.0	0.0	14.4
Benzo(a)pyrene	2.4	2.4	0.0	127.6	729.3	0.0	0.0	2.3	3.6	1.6	61.4	0.0	0.0	1.5	20.3	7.9	0.0	0.0	0.0	0.0	4.4
Benzo(b+j)fluoranthene	6.1	4.1	0.0	67.4	430.7	36.0	0.0	6.6	12.9	3.5	49.0	0.0	0.0	0.0	27.2	14.7	0.0	6.8	34.3	0.0	10.6
Benzo(e)pyrene	6.5	2.7	2.5	83.8	435.3	37.3	0.0	7.3	12.3	2.0	38.6	0.0	0.0	17.3	23.0	16.0	0.0	10.2	17.3	3.9	14.9
Benzo(ghi)perylene	3.6	3.1	9.3	70.0	232.5	0.0	0.0	8.8	4.1	0.0	12.5	0.0	69.0	177.0	5.7	6.7	0.0	19.0	0.0	4.3	106.2
Benzo(k)fluoranthene	2.3	4.1	0.0	11.1	79.8	2.2	0.0	3.3	2.7	0.0	5.8	0.0	0.0	2.7	4.8	4.9	0.0	0.0	7.3	0.0	4.0
Chrysene	25.7	3.0	4.3	256.9	2022.7	216.7	8.2	28.9	66.5	13.5	680.0	0.0	4.4	0.0	102.0	52.0	37.0	9.9	273.3	6.8	31.4
Dibenz(a,j)acridine	0.0	0.0	0.0	12.7	60.8	0.0	0.0	3.4	0.0	0.0	0.0	0.0	3.9	5.5	0.0	0.0	0.0	0.0	0.0	0.0	5.7
Dibenzo(a,h)anthracene	0.0	0.0	0.0	0.0	102.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.0
Dibenzo(a,i)pyrene	0.0	0.0	2.6	9.4	122.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.6
Fluoranthene	5.7	3.0	10.2	34.1	118.3	3.2	0.0	15.9	12.5	88.1	390.0	8.0	1.3	6.9	18.5	9.9	0.0	0.0	7.1	0.0	15.3
Fluorene	73.5	13.5	241.5	272.4	143.9	0.0	2.9	131.6	133.3	1960.0	546.0	3.6	0.0	0.0	99.7	97.0	3.9	0.0	2.0	19.5	25.0
Indeno(1,2,3-cd)pyrene	2.4	3.6	3.0	0.0	60.4	0.0	0.0	3.9	0.0	0.0	0.0	0.0	12.6	17.6	0.0	0.0	0.0	0.0	0.0	0.0	12.9
Naphthalene	368.4	4150.0	756.5	630.7	279.1	0.0	2.1	228.0	292.1	4713.3	880.0	44.4	0.0	7.5	267.7	166.7	6.2	1.4	0.4	796.7	6901.9
Perylene	1.6	2.2	1.4	31.4	147.6	1.6	0.0	2.1	2.9	0.0	15.9	0.0	0.0	3.9	7.6	4.3	0.0	0.0	2.9	1.7	3.0
Phenanthrene	139.8	18.8	356.9	707.9	948.7	6.4	6.3	316.5	461.3	4268.7	5140.0	6.5	18.0	2.7	281.7	246.7	17.5	1.9	43.0	17.5	41.2
Pyrene	42.7	4.1	73.3	308.6	1074.7	20.0	3.5	152.2	51.2	361.8	2260.0	39.4	8.5	85.2	121.3	24.7	37.0	0.0	24.3	13.9	121.3
7H-Dibenzo(c,g)carbazole	0.0	0.0	0.0	0.0	52.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

See Section 14.2 for associated substance CAS numbers.

LEGEND – Crude - Crude Oil; Gas -Gasoline; HFO - Heavy Fuel Oil ; CC Bttm - Cat Cracker Bottoms; Lube Dist. – Lube Distillate; Asphalt - Asphalt (oxidized vs. straight run paving grade); AGO - Atmospheric Gas Oil; VGO - Vacuum Gas Oil; LCO - Light Cycle Oil (cat cracker distillate); HCO - Heavy Cycle Oil (cat cracker gas oil); HC Dist - Hydrocracker Distillate; HCGO - Hydrocracker Gas Oil (covers cracked lube basestock); HC Bttm - Hydrocracker Bottoms; Cat Feed - Cat Cracker Feed; ATB - Atmospheric Bottoms; TC Res - Thermal Cracker Residue (visbreaker); HPVD – Heavy Paraffin Vacuum Distillate; LPVD – Light Paraffin Vacuum Distillate; Jet – Jet Fuel; Arom - Aromatic Extract Streams (heavy distillate extract, pole oil).

Note - Solvent extracted (straight run) lube basestock results were all below detection limits.

Sources

Canadian Petroleum Products Institute (CPPI). 2011. Codes of practice for developing an emission inventory for refineries and terminals. Rev. 13. Accessed at [canadianfuels.ca/userfiles/file/CPPI_CoP_Rev13_Revised_for_Selenium\(1\).pdf](http://canadianfuels.ca/userfiles/file/CPPI_CoP_Rev13_Revised_for_Selenium(1).pdf) on July 18, 2014.

Appendix C: Speciated emissions from distillate oil storage tanks

This speciation is from SPECIATE version 4.4 (2014a).

Compound	CAS number	% (by mass)	Molecular Weight
1,2,4-trimethylbenzene (1,3,4-trimethylbenzene)	95-63-6	0.37	120.1916
Benzene [#]	71-43-2	2.57	78.11184
Cyclohexane	110-82-7	1.23	84.15948
Ethane*	74-84-0	2.13	30.06904
Ethylbenzene [#]	100-41-4	0.32	106.165
Isobutane	75-28-5	7.34	58.1222
Isopropylbenzene (cumene) [#]	98-82-8	0.05	120.1916
N-butane	106-97-8	28.08	58.1222
N-heptane	142-82-5	1.7	100.2019
N-hexane [#]	110-54-3	5.61	86.17536
N-nonane	111-84-2	0.04	128.2551
N-octane	111-65-9	0.01	114.2285
N-pentane	109-66-0	7.97	72.14878
O-xylene [#]	95-47-6	0.13	106.165
Propane	74-98-6	12.7	44.09562
Toluene [#]	108-88-3	2.06	92.13842
Unidentified	N/A	27.69	137.1921

*not a VOC

[#]HAP

Data are from

Fujita, E.M., Lu, Z., Sagebiel, J.C., Watson, J.G. Apportionment for the Coastal Oxidant Assessment for Southeast Texas. Desert Research Institute, Reno, NV. Prepared for Texas Natural Resource Conservation Commission, Austin, TX. 1995

and are a composite of nine emission profiles from distillate oil storage tanks as measured in 1993. SPECIATE contains no assessment of the uncertainty in these values or of the analytical methods used and does not include any information about controls.

Sources

US Environmental Protection Agency (US EPA). February 2014a. SPECIATE version 4.4. Accessed at www.epa.gov/ttn/chief/software/speciate/speciate4/speciate4_4_final.zip on August 3, 2014.

Appendix D: Tank description discrepancies in TCEQ DIAL study

The report for the Texas Commission on Environmental Quality’s DIAL study (TCEQ 2010) says that the emissions of VOCs from tanks holding fuel oil (referred to as fuel oil No. 6 in Table 3 in the TCEQ DIAL report) of unknown freshness were found to be low at less than 1 lb/hr to 15 lb/hr, despite the fact that the tanks were heated (TCEQ 2010). However, none of the tanks listed in Attachments C1 and C2 of Appendix B in the TCEQ DIAL report are characterized as heated and none are characterized as holding fuel oil No. 6.

The descriptions of the storage tanks in the main body of the TCEQ DIAL study report (TCEQ 2010) and the descriptions in Appendix A, Appendix B, and attachments C1 and C2 of Appendix B of that report have some discrepancies as well as some consistencies. In particular, it is not clear which tanks, if any, were heated, and how tanks were designated as holding fuel oil. It could be argued that none of the liquid stocks listed in attachments C1 and C2 would be stored in a heated tank; the heaviest is raw furnace oil which would have a kinematic viscosity of 7.35 to 11.75 cSt at 40°C. Given a density in the range of 0.88 to 0.90 g/ml, the dynamic viscosity at 40°C (104°F) is at most 0.011 Pa-s. Using the BASIC program given in the intermediate streams section of this report, the estimated viscosity at 27°C (roughly ambient temperatures) is at most 0.016 Pa-s, well below the 2 Pa-s viscosity guideline for determining the minimum pumping temperature.

The following table summarizes a few tank characteristics from these sections of the TCEQ DIAL study report.

Characteristic	Main body of report	Appendix A	Appendix B (excluding attachments)	Attachments C1 and C2
# of tanks described	37			37
# of heated tanks	At least 2	At least 2	At least 7	zero
Tank contents	Gasoline (4 tanks), crude oil, diesel, fuel oil (at least 2 tanks holding fuel oil, described as fuel oil No. 6 in Table 3); sometimes naphtha is included in this list	Gasoline, crude oil, fuel oil, naphtha, distillate		Naphtha (5 tanks), light cat naphtha (3 tanks), gasoline (4 tanks), kerosene (2 tanks), crude oil (7 tanks), out of service (4 tanks), LCCO* (10 tanks), butanol (1 tank), furnace oil** (1 tank)

*The acronym LCCO is not defined in the report but almost certainly refers to light catalytic cycle oil.

This is also known as light cycle oil, LCO, FCCU LCO, FCCU light cycle oil, fluid catalytic cracker unit light cycle oil, catalytic-cracked light gas oil, middle distillate cutter oil, untreated diesel fuel blending component, light catalytic cracked distillate (petroleum), and C9-C25 petroleum hydrocarbons. In Appendix C of the report, at least two of the tanks holding LCCO were identified as diesel storage tanks. Diesel tends to be a little lighter than LCCO.

**Synonyms for furnace oil are light gas oil, light vacuum gas oil (petroleum), LVGO, vacuum tower light gas oil, intermediate vacuum distillate, vacuum tower intermediate distillate, light paraffinic vacuum distillate, olefins plant feed – heavy, OPF-heavy, LGO stream from a vacuum still, untreated, unrefined, or raw No. 4 fuel oil, unfinished heavy heating oil, burner fuel, C12-C30 petroleum hydrocarbons.

Kerosene is sometimes called fuel oil No. 1 and is the fraction in between gasoline and diesel. It is used as jet fuel. Butanol is an alcohol with four carbon atoms. Neither of these streams could be described as gasoline, crude oil, diesel, or fuel oil No. 6.

The main body and Appendix A of the report don't usually identify the tanks and their contents by tank ID, and usually don't identify the number of tanks holding each category of fluid. It appears that perhaps the terms LCCO, distillate, and diesel were used interchangeably. The gasoline and crude oil tanks seem to be uniformly defined throughout. Perhaps the terms kerosene, furnace oil, fuel oil/fuel oil No. 6, and light cat naphtha were also used interchangeably.

Sources

Texas Commission on Environmental Quality (TCEQ). March 29, 2010. Differential absorption lidar study, final report. Accessed at www.tceq.texas.gov/assets/public/implementation/air/am/contracts/reports/ei/DIAL.pdf on July 23, 2014.