## Project Title:

Fire Exposure of Low Volatility Liquids, Rev. 9, October 16, 2018

## Problem Statement:

Pressure relief valve sizing due to vapor generation for vessels containing boiling liquids during a pool fire scenario typically involves several assumptions:

- The vessel is isolated during the fire in order to simplify the analysis (API 521).
- The amount of heat absorbed by the liquid inventory is defined by API Standard 521 heat absorption equations. (Refer to API Standard 521, 6th Ed., section 4.4.13.2.4.2, equations 6, 7 and 8.)
- If vaporization (boiling) at relief pressure is predicted below 900°F (482°C), an estimated latent heat of vaporization of the boiling liquid and the appropriate molecular mass of the fraction vaporized are used below the cracking temperature to calculate the pressure relief requirements (absorbed heat divided by latent heat).
- Note that 900°F in the previous bullet item is just an arbitrary round up. This dynamic event is rough and varies. But, as these heavy HCs progress above 800°F and heat is further added, there is a transition from vaporization (boiling) controlled vapor generation to cracking controlled vapor generation. Since these guidelines advise use of a cracking gas temperature of 825°F, 900°F here is a rounded-up higher number. This part of the guidelines advises that if the process model is predicting boiling at or below 900°F, that it is acceptable to stick with the boiling approach commonly used.

The API Standard 521 6th edition (2014) does not address possible cracking reactions at high temperatures. However, the API Standard 5th edition (2007) states:

- If exposure to fire results in vapor generation from thermal cracking, alternate sizing methods can be appropriate.
- The pressure-relief device may be sized for the products of thermal cracking at a temperature at which the decomposition occurs.

Guidelines for pressure relief valve sizing due to vapor generation for vessels containing a non-volatile liquid experiencing thermal cracking are not currently available. This project considers the effects of thermal cracking reactions of selected classes of materials on pressure relief requirements.

## Objective:

When fire-case predicted relief temperature (at relief pressure) exceeds 825°F, the possibility of endothermic thermal cracking reactions instead of or in addition to liquid vaporization as a means of generating vapor must be considered in relief system sizing. The objective of this project is to develop and publish guidelines to address the impacts of thermal cracking in pressure relief valve sizing. These guidelines are intended for use with heavy hydrocarbon materials similar to those typically found in petroleum refining operations. For those materials, the model is conservative for both straight run as well as cracked stocks. Application to other liquids such as hot-oil-belt fluids, lube oils, bio-diesel, *etc.* may be shown appropriate via additional lab testing. On the other hand, some liquids decompose exothermically. These guidelines are not to be used for such systems. The guidelines include a simple model which can then be entered into computer simulation and/or analysis of test data to size pressure relief systems. The guidelines also include a description of the range of model applicability.

Cautionary statement: Similar to supercritical fluids and gas-filled vessels, a model may be developed to predict a required vapor volumetric relief rate for the external fire case. However, this is often done to satisfy ASME Code, NFPA or API requirements. It is important to understand that such systems will also experience elevated and increasing temperatures when exposed to external fire. A PSV will not do much, if anything, to limit temperature rise. For systems like this, those managing overall risk **must consider applying additional layers of protection (LOP) to avoid loss of containment in fire conditions**. The issue of concern is loss (or reduction) in mechanical strength of the vessel walls as metal temperature rises. See API Standard 521, 6th Ed., section 4.4.13.2.3 for a time-to-failure analysis for these conditions.

## Justification:

Guidelines for sizing and selection of pressure relief valves for vessels containing low volatility liquids that experience endothermic thermal cracking reactions in a pool fire are lacking. This project provides guidelines for ERS sizing of these systems exposed to pool fires.

Currently, estimation of the required relief rate in systems experiencing thermal cracking requires detailed kinetic modeling and/or experimental testing. A simple model to generate defensible and technically correct pressure relief valve sizing bases in order to comply with code rules requiring fire-sized pressure relief devices will provide for efficient use of resources. This project provides guidelines and a simple model.

## Approach:

A committee of five voluntary members planned the project, collected and analyzed relevant data, developed a simple model, established a range of validity for the model, developed guidelines for selecting model parameters, and published a final project report. A literature review of thermal cracking data, some kinetic modeling, consulting with process experts and some modest experimental testing (DSC) was used to validate the model. The model parameters are available for the user to modify if the fluid composition varies from the model basis and experimental data are available for the fluid composition in question.

The proposed procedure and model is:

- Calculate heat input using API Standard 521 equations; for example:
  - $\mathbf{Q = C * F * A_{WS}^{0.82}}$ where:
  - Q is fire heat input in BTU/hr
  - C is a constant (21000 or 34500; see API for explanation)
  - F is the environmental factor; see API
  - $A_{WS}$ is the vessel total wetted surface area in square feet
- Use 75 BTU/lb as λ, a conservative endothermic heat of reaction. This is a conservative lumped parameter that includes the reaction and phase transition energies.
- Select a relieving temperature (825°F for typical refinery streams because the endothermic heat of reaction increases at higher temperatures)
- Select a relieving molecular weight and heat capacity ( MW = 100 because that is typical or at the low end of the range of MW of gas evolving from a coker)

- Calculate the required relief vapor rate using the proposed model and fire heat input; a simple example is:
- **W = Q/λ** where
    - Q is fire heat input in BTU/hr
    - λ is the endothermic reaction heat above in BTU/lb
    - W is required relieving rate (vapor) in lb/hr
- and then determine required relief device size using API Standard 520 equations
- Reaction kinetics are conservatively assumed to be such that reaction rate is limited only by external heat addition; this was compared to a kinetic model developed by Harold Fisher (email reference 2) using the detailed thermal decomposition analyses and test results in reference 1. Results of the comparison support the above model as conservative.

The model may be applied based on the assumption the required relief rate can be predicted assuming the vessel fluid has the properties of a typical LGO or heavier refinery stream.

Model documentation includes an explanation of the range of applicability, a Precautionary Statement, and notes that the model is expected to be conservative. Where the relief device size is controlled by other scenarios, the documentation is complete (1). Where the relief device size is controlled by this scenario and an existing relief device is shown adequate by this model, the documentation is complete (2). Where the relief device size is controlled by this scenario and an existing relief device is shown inadequate by this model, it may be necessary to conduct further testing to show less conservatism is justified (3). This paragraph states an important justification for this guideline. If either of the first two statements are true, simple documentation is generated and technical resources can then be applied to more complex issues elsewhere. Detailed modeling and testing are then only required if statement 3 is true.

## Test Results / Support:

Lab testing and results (Reference 3) support the above model:

| DSC Test ID | Oil tested | Estimated endothermic Rxn heat, BTU/lb | DSC Scan Rate, °C/min | Reaction Temperature Range, °C | Endothermic Peak, °F |
|---|---|---|---|---|---|
| DSC1 | Mineral Oil | 108 | 10 | 352 - 485 | 905 |
| DSC2 | Mineral Oil | 77 | 10 | 417 – 481 | 898 |
| DSC3 | Hydrotreated Gas Oil | 126 | 2 | 415 – 460 | 859 |
| DSC5 | Gas Oil #1 | 99 | 2 | 375 – 447 | 836 |
| DSC7 | Gas Oil #2 | 121 | 2 | 370 – 448 | 838 |
| DSC9 | Heavy Coker Gas Oil | 89 | 2 | 372 – 445 | 834 |
| DSC11 | Heavy Vacuum Gas Oil | 106 | 2 | 376 - 441 | 826 |

These DSC data provide a close approximation of what the relief system model temperature is. The 825°F in this model is close to the endothermic peak temperature observed in the DSC plots. This is the point of maximum endothermic reaction in the experiment. Fire exposure to commercial size equipment typically results in imposed heat up rates of 2 to 10°C/min - the same rates as used in the DSC experiments. This improves the validity of basing the model on these DSC runs. In an actual fire exposure scenario, the endothermic heat flow of the reaction would tend to decrease this temperature rise rate as the reaction rate becomes significant at high temperatures. In fact, that is why this model is conservative as it assumes that the temperature rise rate is zero; all the fire heat input goes into reacting/breaking these molecules. In the DSC experiments the temperature rise rate does not decrease because of the way the experiment is performed and the endothermic peak (minimum point on the DSC plot) is "driven" to a slightly higher temperature than would occur in the fire exposure scenario. This slightly higher peak temperature observed in DSC experiments would be even more conservative to use in the ERS design model. This additional level of conservatism is not needed considering the primary purpose of this model. However, for relief design purposes, it would be acceptable for smaller vessels which have a higher surface area to volume ratio and are heated more rapidly by fire exposure to use a higher sizing temperature (around 900°F).

The above model and lab results are corroborated by emails obtained from a refinery coking expert (Reference 4).

The committee also conducted theoretical calculations of endothermic reaction heat based on textbook values for long-chain HC heats of formation. These calculations resulted in much higher theoretical endothermic reaction heats than presented in this model. The values generated and method are shown in Appendix 3.

## Appendices:

1. Sample DSC Output
2. Description of Calorimeters
3. Theoretical Reaction Heat Calculations

## DIERS Committee:

Duties of all committee members include:

- Execute assigned tasks and gather information and results on time
- Present the gathered data for group discussion
- Evaluate each other’s results in terms of physicality and application ranges
- Write portions of the Guideline

Specific roles and responsibilities include:

| Member | Roles | Responsibilities and contribution |
|---|---|---|
| John Hauser | Project Manager | 1. Obtain and review literature data from G.E.Melhem and H.G.Fisher<br>2. Arrange lab tests as required<br>3. Develop, revise and present report |
| Dustin Smith | Vice Project Manager | 1. Jointly review lab test results with J.J.Hauser and agree on net and conservative average endothermic $\Delta H_{RXN}$ |

| | | |
|---|---|---|
| Dan Smith | Thermodynamics expert | 1. Conduct specified lab tests |
| Greg Hendrickson | Operating Committee Liaison | 1. Report project progress to DIERS and AIChE committees<br>2. Represent DIERS stake on the project<br>3. Provide peer review of Project Guideline |
| Marc Levin | Technical Review | 1. Review report and data. Provide technical guidance. |
| | | |

## Contacts:

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| Greg Hendrickson | hendrgg@cpchem.com | (281) 359-6592 |
| Marc Levin | marc.levin@wsu.edu | (509) 335-6836 |

## References:

1. “Establishing the Maximum Carbon Number for Reliable Quantitative Gas Chromatographic Analysis of Heavy Ends Hydrocarbons”, PhD Thesis of Diana Margarita HERNANDEZ BAEZ, Heriot-Watt University, Institute of Petroleum Engineering, March 2013.
2. Private email from Harold Fisher to John Hauser, 24 March 2017.
3. Personal correspondence. Heavy Oil Cracking Hazards. A summary of test results submitted by Dan Smith, June 12, 2017.
4. Private emails between Mike Kimbrell and John Hauser, January, 2018.
5. “Chemistry of Catalytic Processes”, Gates, Katzer, and Schuit, McGraw-Hill (1979)
6. ”Thermal Cracking of Kerosene”, van Camp, van Damme and Froment, Ind. Eng. Chem. Process Des. Dev. (1984, 23, 155-162)

# Appendix 1
# Description of Calorimeters

### *Differential Scanning Calorimetry (DSC)*

Preliminary thermal stability tests with heavy oils were conducted with TA Instruments Models 2000 and 2500 Differential Scanning Calorimeter modules. The experiments were conducted with heavy-walled M20 gold plated crucibles from the Swiss Institute of Security and Safety or with equivalent crucibles available from Mettler Toledo. These crucibles are capable of withstanding about 200 bar of internal pressure once properly sealed.

The crucibles were carefully weighed before and after each experiment to ensure that no mass was lost during the experiment. The instrument was calibrated at each ramp rate using high-purity metal calibration standards. The Q2000 uses a four point method for temperature calibration using gallium, indium, lead, and zinc; the Q2500 only requires indium. Both instruments use the melt of indium to calibrate the enthalpy value.

The accuracy of the melt enthalpy is less than 1% for indium (measured at 156.6°C). The instrument accuracy of the heat flow measurement at higher temperatures was not quantified. Heats of reaction integrations of DSC data are likely to have significantly more error due to the subjective nature of the selection of integration bounds.

### *Pressure Screening Tool (PST)*

The pressure screening tool is a custom-built reactive hazard screening test utilized to detect the generation of non-condensable gas. The test is used for quick preparation of residue and gas samples for analysis, determination of pressure generation potential, and determination of condensing curves of the reaction intermediate or final reaction products. The apparatus consisted of a closed 9.25 mL spherical test cell placed inside of a cylindrical aluminum tube fitted with an electric heater and thermocouple. The closed test cell is fitted with a 1/32-in diameter thermocouple and an oil-filled pressure transducer to measure temperature and pressure of the sample during the experiment. The test cell and heater assembly are placed inside of an autoclave to provide protection from shrapnel in the event of a bomb rupture. Tests are not conducted without prior DSC screening. A high pressure interlock is included to stop heating if excessive pressure is reached. A typical assembly of the PST is shown in Figures 1 and 2.

Typical operation involves approximately 3 g of sample loaded into the test cell in a nitrogen-purged dry box. The temperature of the aluminum heater tube is increased at a constant ramp rate of 1 to 2°C/min while the temperature and pressure of the sample are recorded. After the desired maximum temperature is reached the heater is turned off and the sample is allowed to cool back to ambient temperature.

Figure 1. PST Sample Bomb and Sensing Assembly

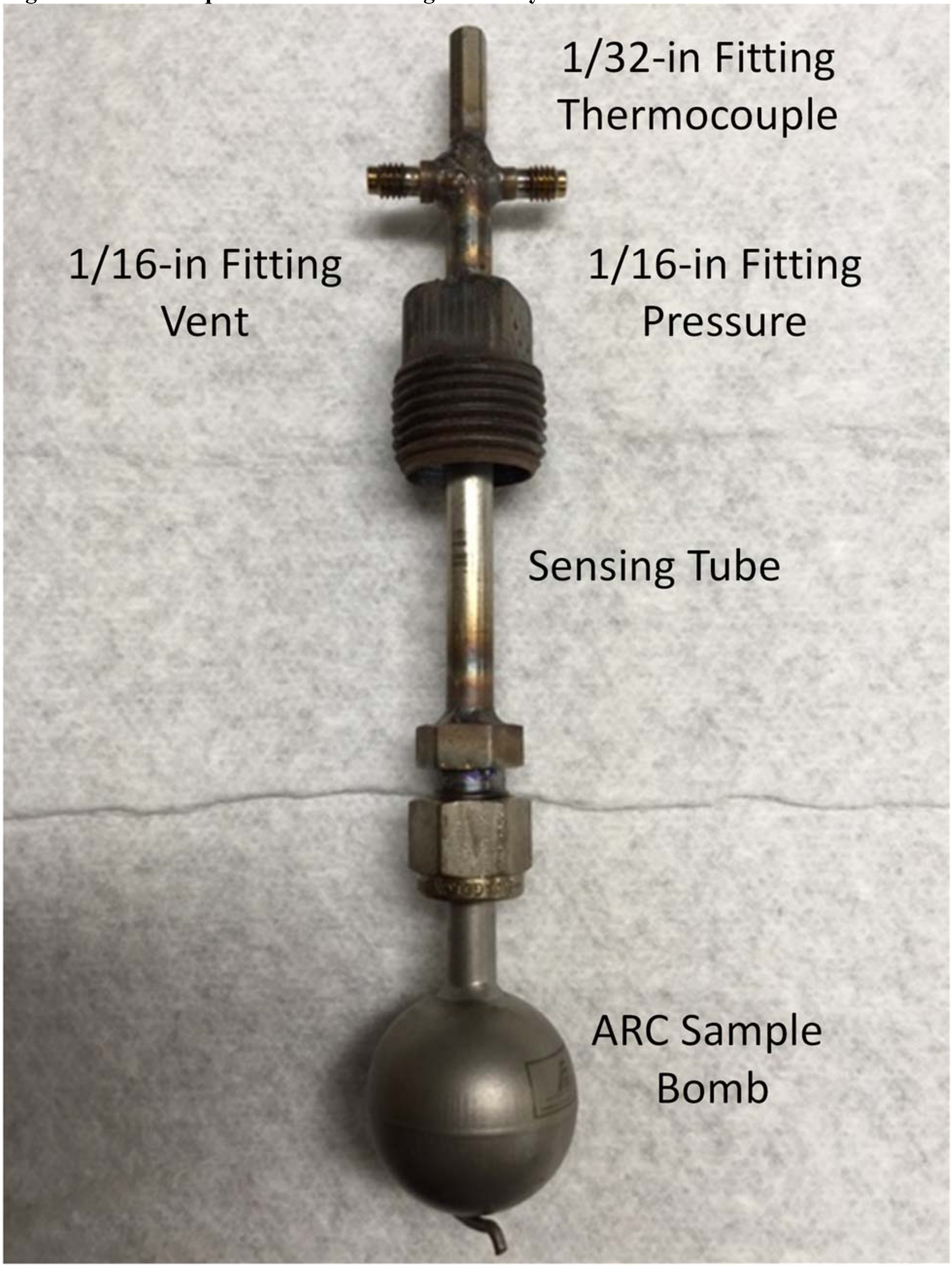


**Figure 2.  PST During Operation**

# Appendix 2
# Sample DSC Output

Mineral oil was tested by DSC, TGA, and PST to better understand the high temperature endothermic decomposition (cracking) that occurs with this material.

Interest in this high temperature decomposition is to measure the extend of gas generation that might occur as a result of the high temperature endothermic (cracking) that might occur as a result of fire exposure to a mineral oil containing vessel. DSC and PST data are shown below.

DRAKEOL 35 Mineral Oil is assumed to have a molecular weight equivalent to a C34 alkane. DSC data suggests that the heat of reaction is +250.3 J/g (+119.87 kJ/gmol). The closed DSC data also appears to indicate the possibility of an exothermic reaction occurring after the endothermic cracking reaction.

The endothermic reaction is well matched by a 1st order kinetic model with a rate constant described by the following Arrhenius rate expression.

$$k = (4.47 \times 10^{18}) exp(-35968/T)$$

Where $T$ is kelvin and k is in $s^{-1}$. The high activation energy determined by regression of the data to a 1st order model may suggest that the mechanism is more complicated than the assumed 1st order model and possibly autocatalytic.

**Figure DSC1.  DRAKEOL 35 Mineral Oil.**

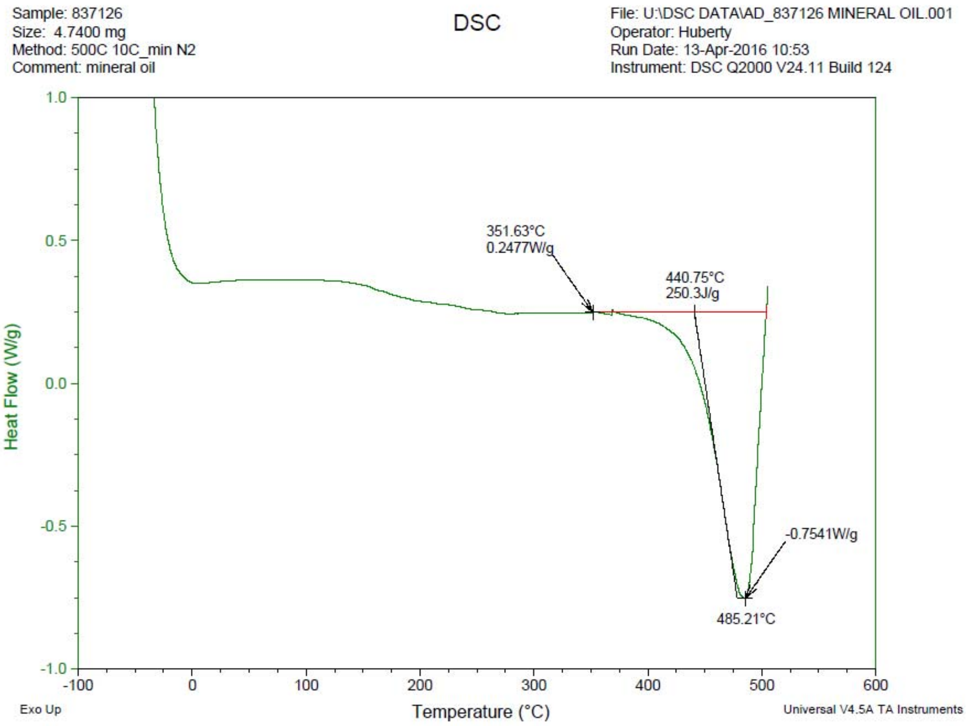


**Figure DSC2.  DRAKEOL 35 Mineral Oil.**

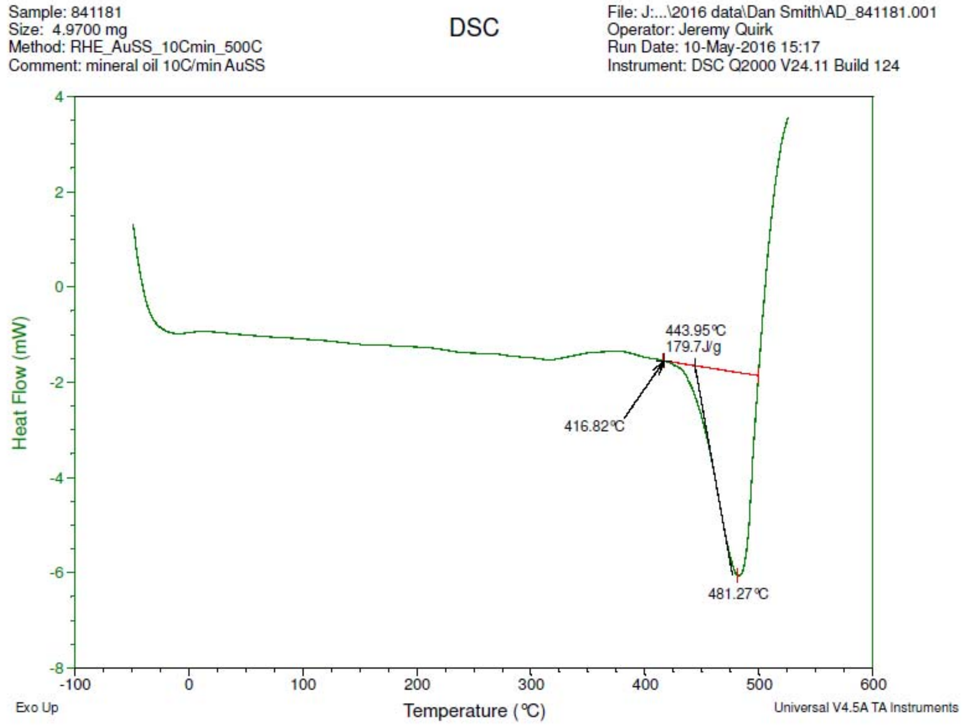
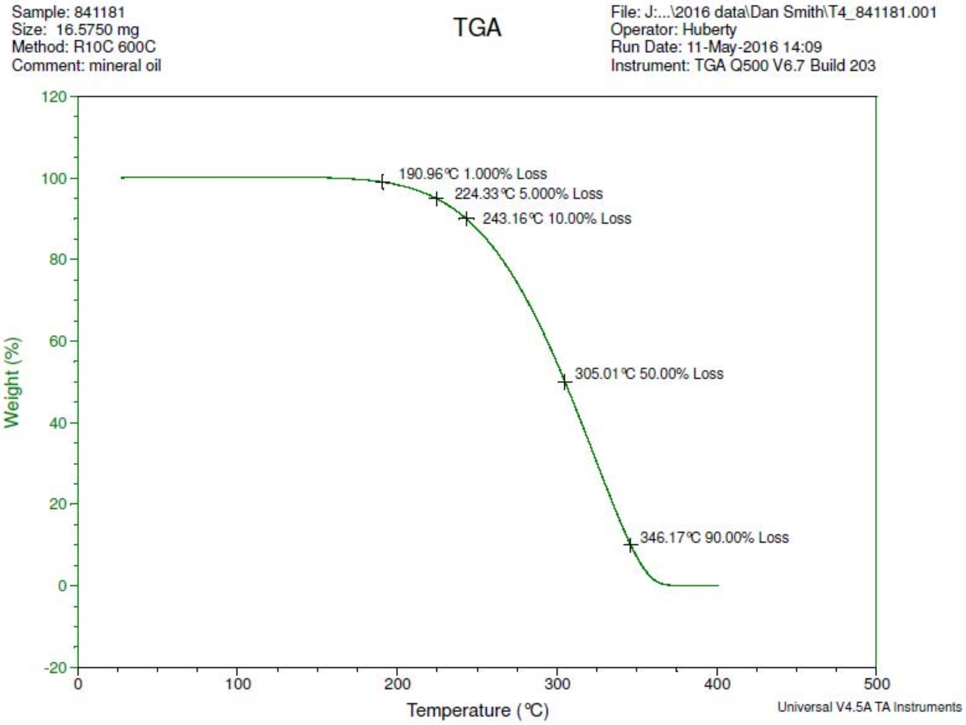


Figure TGA1. DRAKEOL 35 Mineral Oil.



Sample: 841181
Size: 16.5750 mg
Method: R10C 600C
Comment: mineral oil

File: J:...\2016 data\Dan Smith\T4_841181.001
Operator: Huberty
Run Date: 11-May-2016 14:09
Instrument: TGA Q500 V6.7 Build 203

**Figure PST1a.  Differential Temperature and Pressure versus Sample Temperature (PST20160421)**

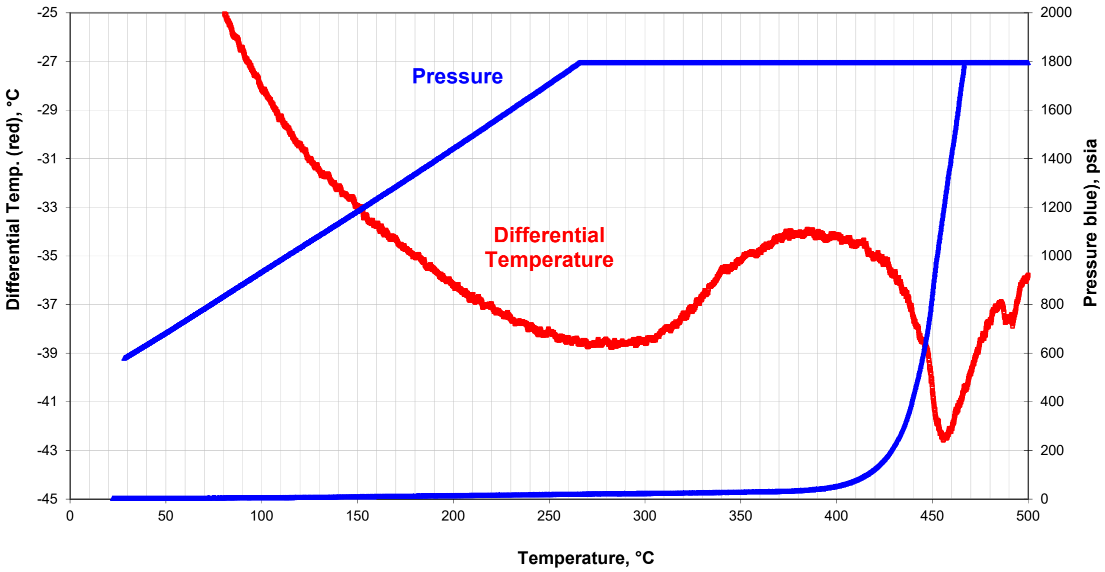
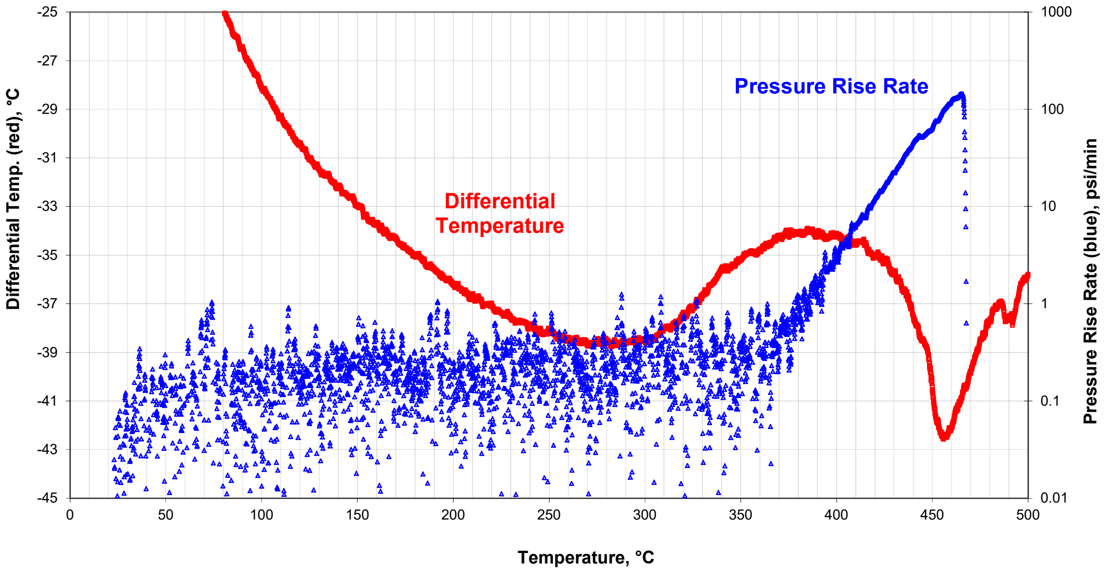


**Figure PST1a.  Differential Temperature and Pressure Rise Rate versus Sample Temperature (PST20160421)**



PST experiment PST20160421 was conducted with 3.17 g of mineral oil (0.006618 gmols) charged into the 9.25 mL.  The final pressure after cool down was 564.5 psig at 28.27°C.  After cool down and venting 1.19 g of material was recovered.  Assuming the difference represents the non-condensible gas (1.98 g)(0.0707 gmols ethylene) moles of gas is on the order of 14.11/1000=0.01411 or 2.13 mol per mol of mineral oil.

Figure PST1a. Differential Temperature and Pressure versus Sample Temperature (PST20160426)

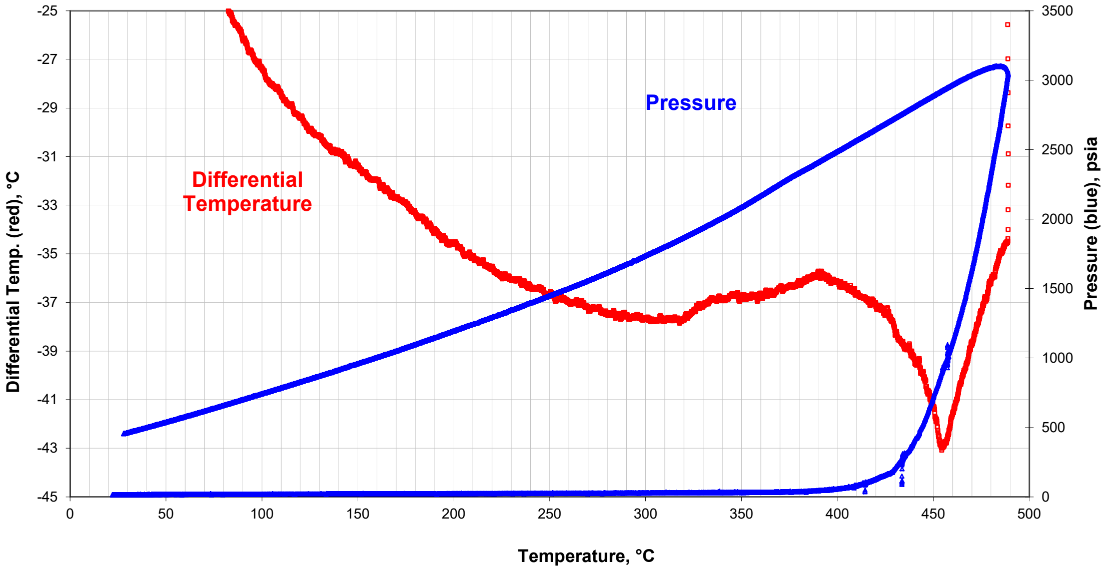
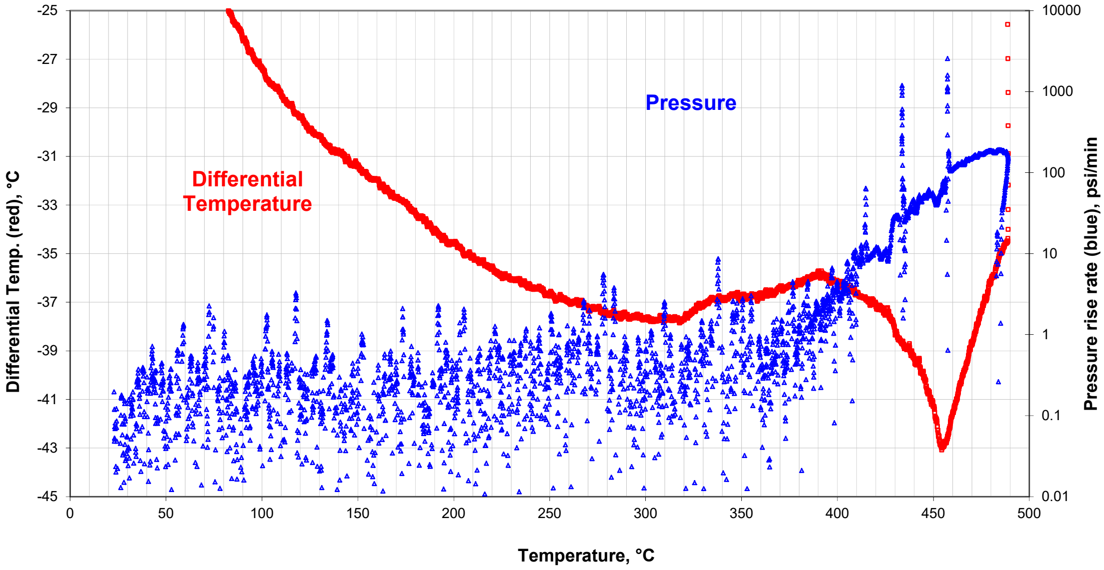


Figure PST1a. Differential Temperature and Pressure Rise Rate versus Sample Temperature (PST20160426)



PST experiment PST20160426 was conducted with 3.09 g of mineral oil charged into the 9.25 mL. The final pressure after cool down was 439.9 psig at 27.95°C. After cool down and venting 1.15 g of material was recovered.

Additional DSC experiments were conducted with Refinery streams. DSC experiments were conducted with ramp rates of 2 and 10°C/min. DSC results are shown below.

In some cases the selection of the DSC onset temperature (deviation from the established baseline) is difficult to determine. Typically, selection of the onset temperature is subjective and is based on the analyst's opinion. For example endothermic deviations from the base heat flow in Figure DSC4 are observed at points labeled A, B, and C. Similar heat flow behavior is observed in many of the test results. This could be an indication of different reactions or reaction mechanisms. In all cases the onset temperature for heat flow integration was selected near the point labeled B, but it could have been selected at the other points – more information is needed to make a better selection.

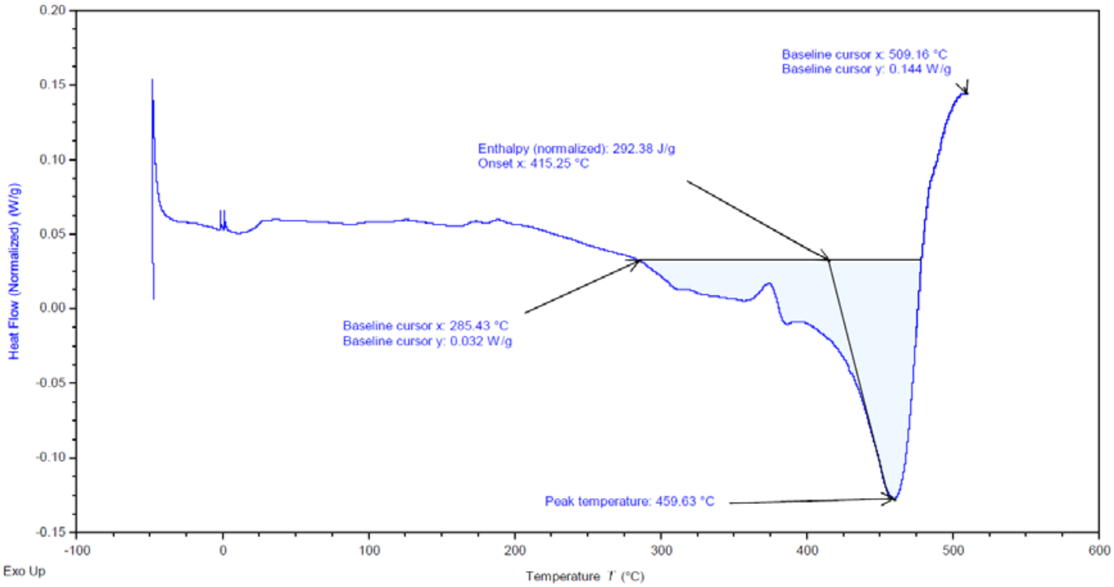
It is expected that the peak temperature and onset temperature will be shifted to lower temperatures with lower experiment ramp rates. The peak temperature is a more consistently shows this effect.

Previous DSC experiments with mineral oil appear to show an exothermic heat flow following the high temperature endothermic cracking. Some of the 2°C/min ramp DSC experiments with the refinery streams also show what appears to be an exothermic heat flow after an initial endothermic heat flow. This could be evidence of a high temperature reaction, or it is also possible that a shift in the baseline is occurring due to the change in heat capacities of the reaction products versus the reaction reactants. The experiment was terminated before the heat flow established a baseline level.

## Figure DSC3. Hydrotreated Gas Oil 2°C/min

Sample: Randy 2C/min 500 C
Comment: 2C/min to 500 C N2
Operator: huberty
File: s:\cref\7 cref projects\mineral oil\experimental data\jim, bob, randy\randy 2cmin 500 c.tri

Instrument/Date: DSC2500,3/29/2017 12:07:33 PM
Sample Size: 6.39000 mg
Pan type: Other



## Figure DSC4. Hydrotreated Gas Oil 10°C/min

Sample: Randy 10C/min 500 C
Comment: 10C/min to 500 C N2
Operator: yochim
File: s:\cref\7 cref projects\mineral oil\experimental data\jim, bob, randy\randy 10cmin 500 c.tri

Instrument/Date: DSC2500,3/28/2017 2:49:36 PM
Sample Size: 6.40000 mg
Pan type: Other

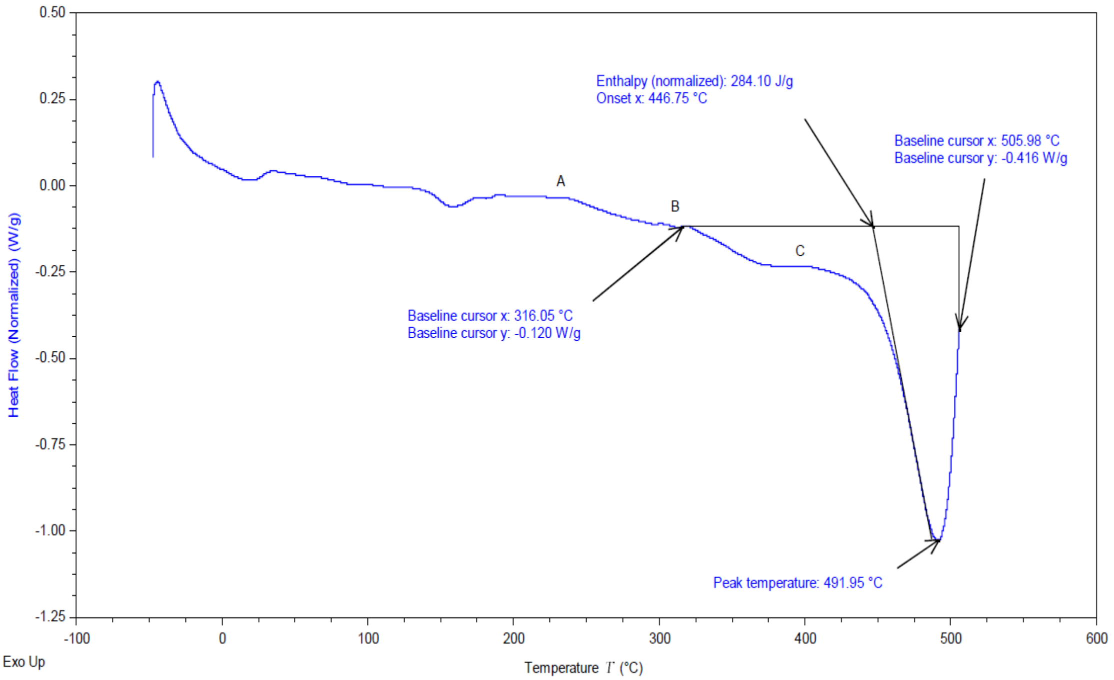


**Figure DSC5. Gas Oil #1 2°C/min**

Sample: Jim 2C/min 500 C
Comment: 2C/min to 500 C N2
Operator: Huberty
File: u:\dsc data\jim 2cmin 500 c.tri

Instrument/Date: DSC2500,3/29/2017 7:13:52 AM
Sample Size: 5.68000 mg
Pan type: Other

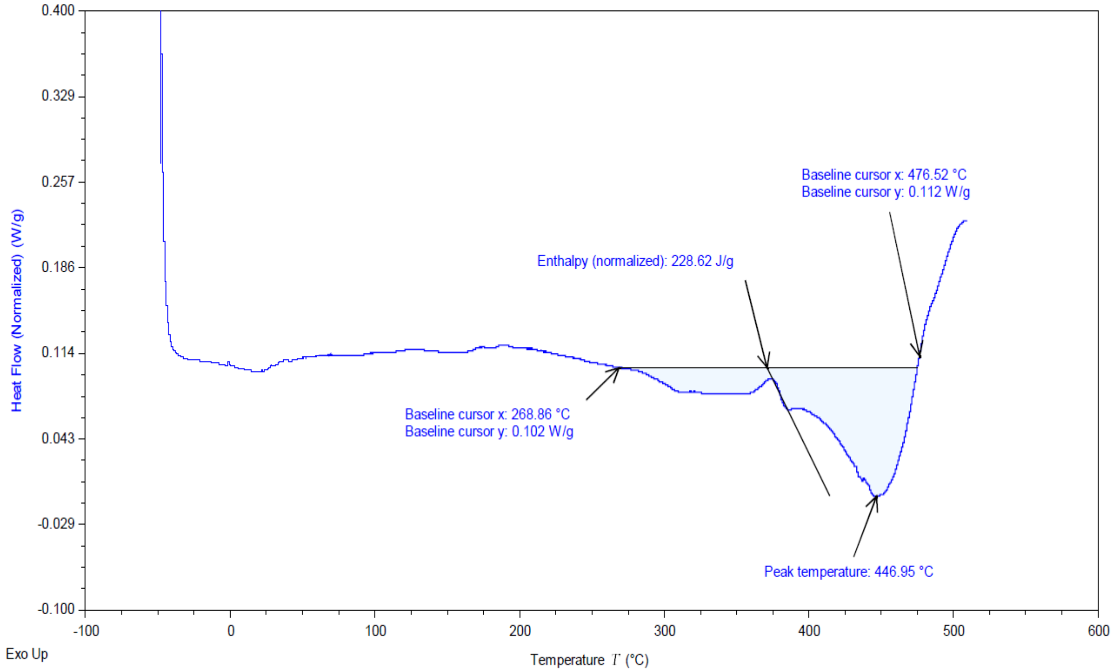
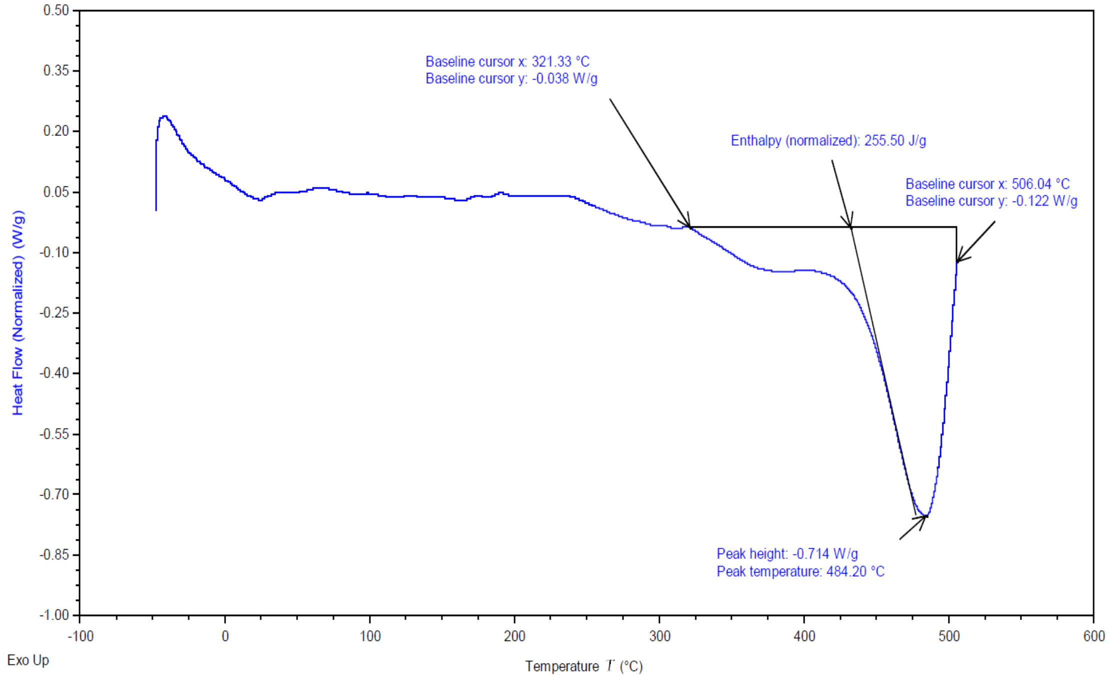


**Figure DSC6. Gas Oil #1. 10°C/min**

Sample: Jim 10C/min 500 C
Comment: 10C/min to 500 C N2
Operator: Huberty
File: u:\dsc data\jim 10cmin 500 c.tri

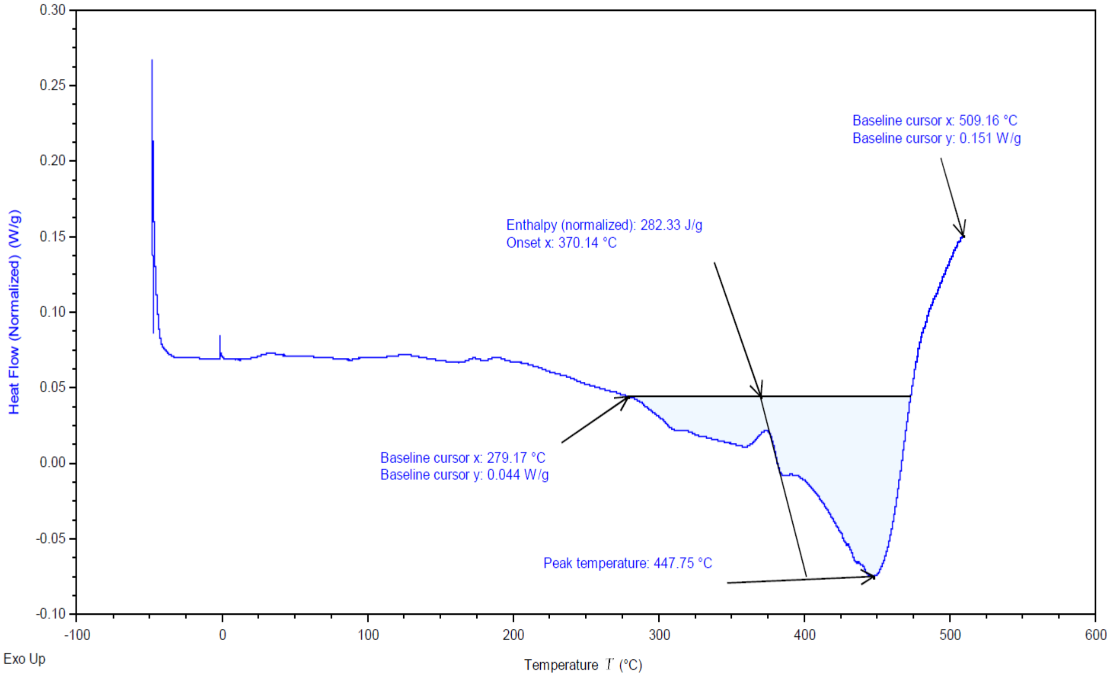
Instrument/Date: DSC2500,3/28/2017 1:40:00 PM
Sample Size: 5.77000 mg
Pan type: Other



## Figure DSC7. Gas Oil #2 2°C/min

Sample: Bob 2C/min 500 C
Comment: 2C/min to 500 C N2
Operator: huberty
File: s:\cref\7 cref projects\mineral oil\experimental data\jim, bob, randy\bob 2cmin 500 c.tri

Instrument/Date: DSC2500,3/29/2017 5:01:47 PM
Sample Size: 6.25000 mg
Pan type: Other



## Figure DSC8. Gas Oil #2 10°C/min

Sample: Bob 10C/min 500 C
Comment: 10C/min to 500 C N2
Operator: yochim
File: s:\cref\7 cref projects\mineral oil\experimental data\jim, bob, randy\bob 10cmin 500 c.tri

Instrument/Date: DSC2500,3/28/2017 3:59:03 PM
Sample Size: 6.16000 mg
Pan type: Other

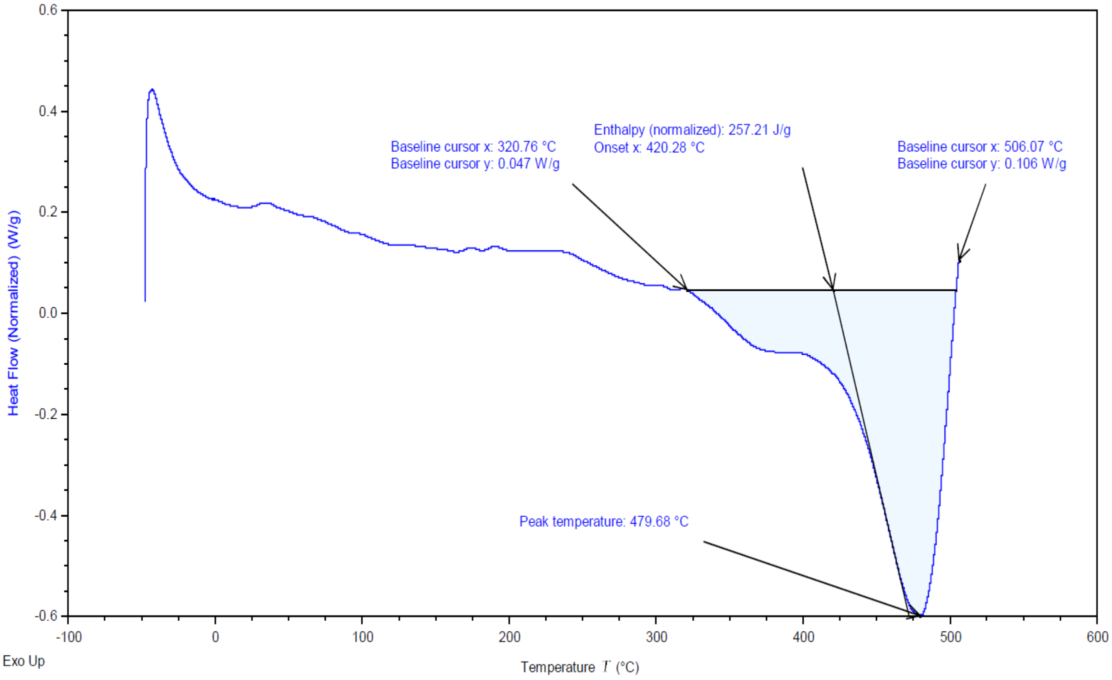


**Figure DSC9. Heavy Coker Gas Oil 2°C/min**

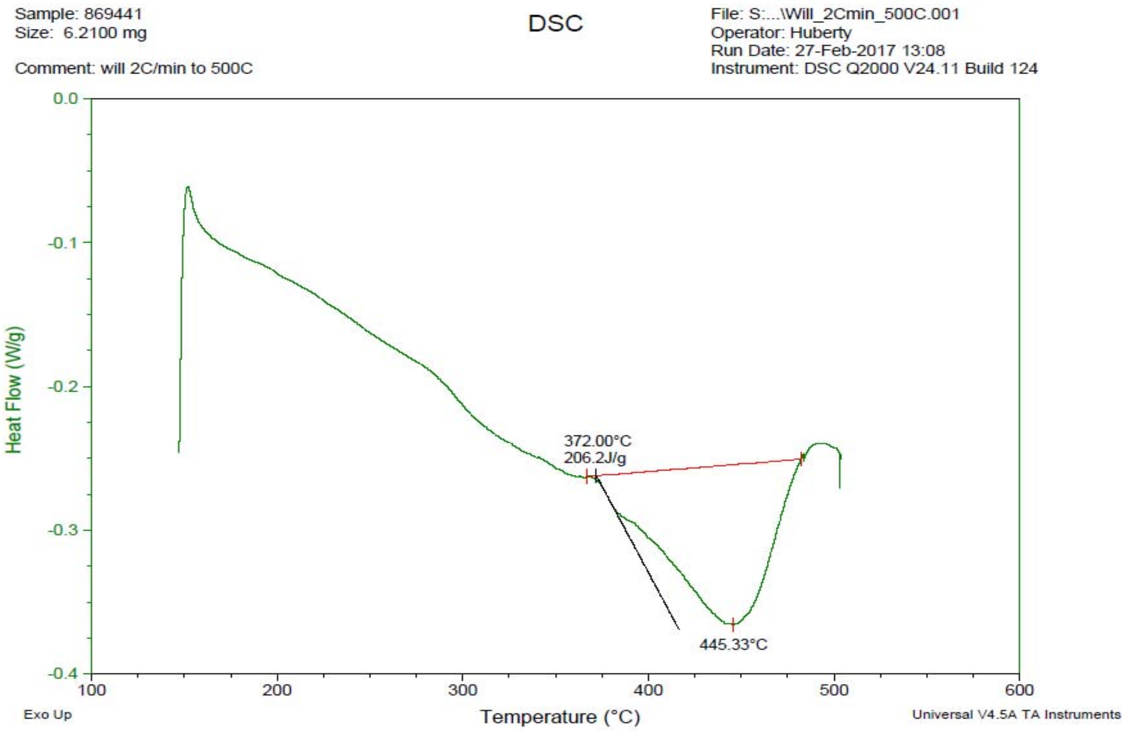


**Figure DSC10. Heavy Coker Gas Oil 10°C/min**

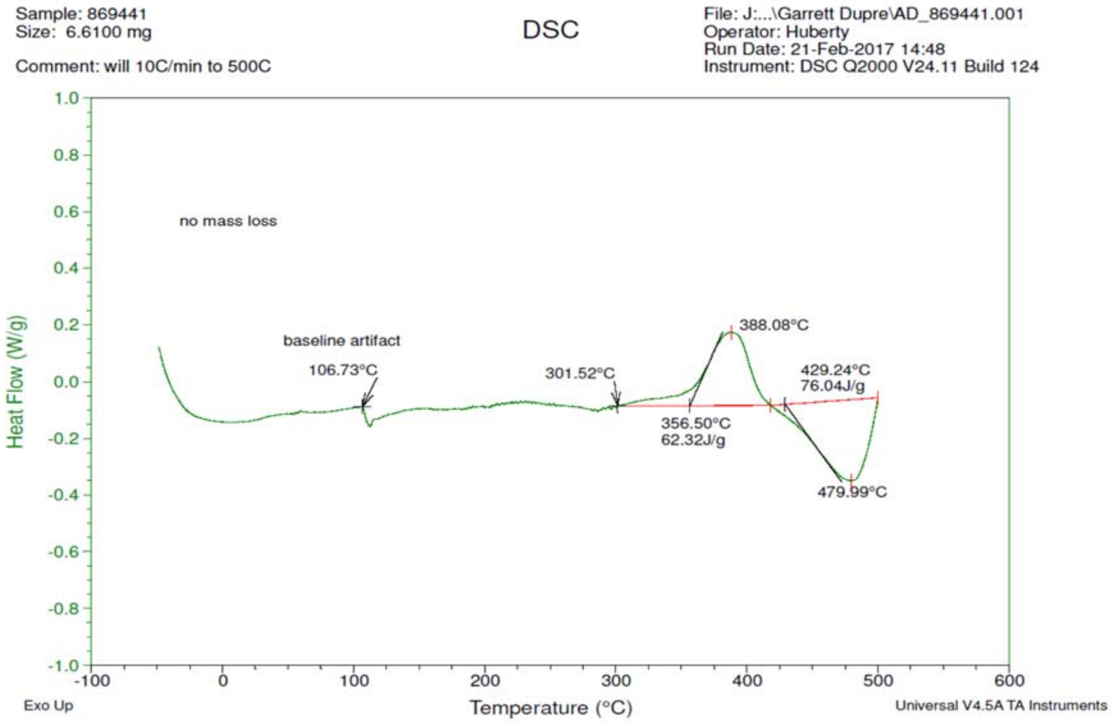


Figure DSC11. Heavy Vacuum Gas Oil 2°C/min

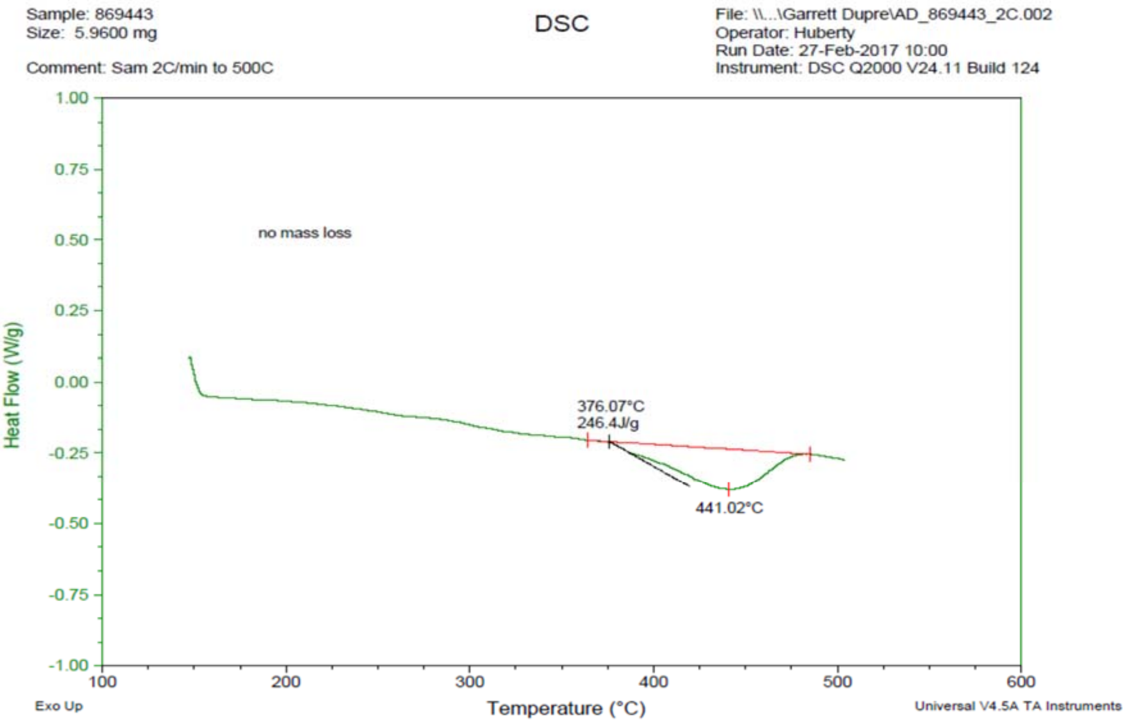
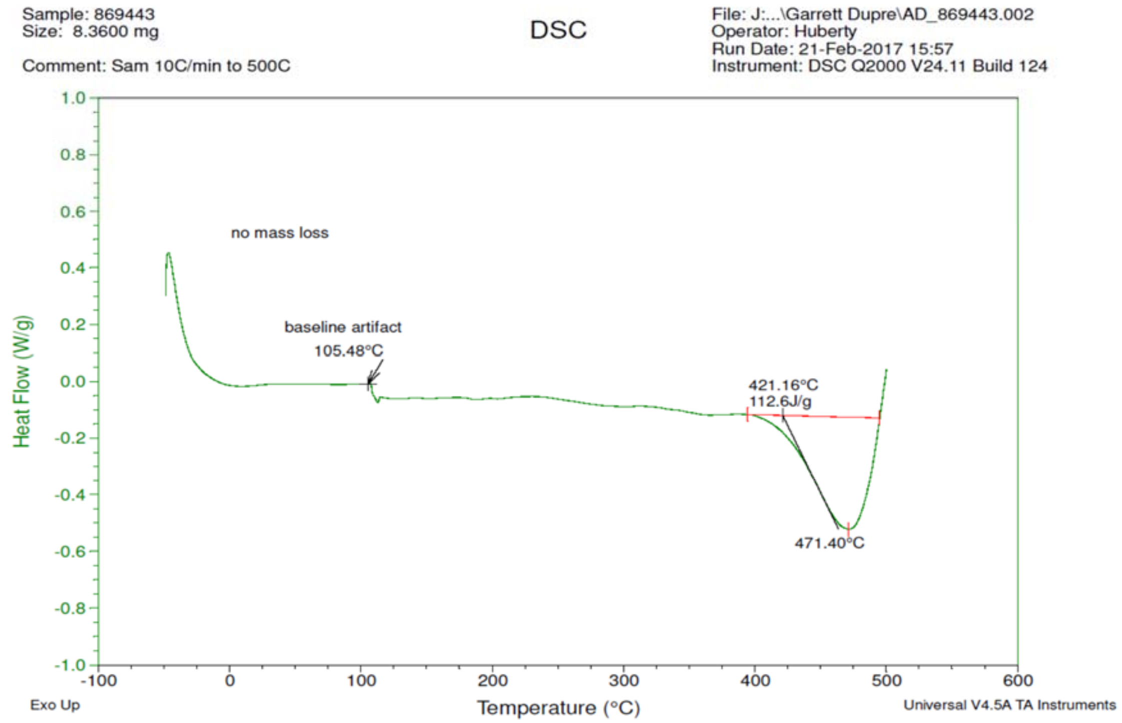


Figure DSC12. Heavy Vacuum Gas Oil 10°C/min



# Appendix 3
# Theoretical Reaction Heat Calculations
## By Dr. Marc Levin

### Hydrocarbon Cracking Heat of Reaction Calculation

| Carbon # | | *Smith & Van Ness (1975), Table 4-4* | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | MW | Standard Heats of Formation [cal/gmol] | | | | $\Delta$hcomb,liq | Reactant Elements | | | C, H Balance in Products | | | | $\Delta H_{rxn,gas}$ | | $\Delta H_{vap}$ | | | $\Delta H_{rxn,liq}$ | |
| | | | (gas) | (gas) | (liquid) | [cal/gmol] | C | H | | C | H | | [cal/gmol] | [BTU/lb] | [J/g] | [J/kmol] | [cal/gmol] | [cal/gmol] | [BTU/lb] | [J/g] |
| ***Cracking of alkane to form ethylene*** | | | | | | | | | | | | | | | | | | | | |
| 0 | 2.016 | H2 (g) | 0 | SVN | | | 0 | 2 | | | | | gas-phase | | | | | liq. reactant | | |
| 2 | 28.1 | C2H4 (g) | 12496 | SVN | | | 2 | 4 | | | | | | | | | | | | |
| 3 | 42.1 | C3H6 (g) | 4879 | SVN | | | 3 | 6 | | | | | | | | | | | | |
| 6 | 86.2 | n-Hexane (g) | -39960 | SVN | | | 6 | 14 | 3 | 0 | 2 | n-Hexane (g) --> 3 C2H4 + H2 | 77448 | 1618 | 3760 | | | | | |
| 8 | 114.2 | n-Octane (g) | -49810 | SVN | | | 8 | 18 | 4 | 0 | 2 | n-Octane (g) --> 4 C2H4 + H2 | 99794 | 1572 | 3655 | | | | | |
| 10 | 142.3 | n-Decane (g) | -59660 | SVN | | | 10 | 22 | 5 | 0 | 2 | n-Decane (g) --> 5 C2H4 + H2 | 122140 | 1545 | 3592 | | | | | |
| 12 | 170.3 | n-Dodecane (g) | -69510 | SVN | | | 12 | 26 | 6 | 0 | 2 | n-Dodecane (g) --> 6 C2H4 + H2 | 144486 | 1527 | 3549 | | | | | |
| 14 | 198.4 | n-Tetradecane (g) | -79360 | SVN | | | 14 | 30 | 7 | 0 | 2 | n-Tetradecane (g) --> 7 C2H4 + H2 | 166832 | 1514 | 3518 | | | | | |
| 16 | 226.4 | n-Hexadecane (g) | -89210 | SVN | | | 16 | 34 | 8 | 0 | 2 | n-Hexadecane (g) --> 8 C2H4 + H2 | 189178 | 1504 | 3495 | | | | | |
| 18 | 254.5 | n-Octadecane (g) | -99060 | SVN | | | 18 | 38 | 9 | 0 | 2 | n-Octadecane (g) --> 9 C2H4 + H2 | 211524 | 1496 | 3477 | | | | | |
| 20 | 282.6 | n-Eisocane (g) | -108910 | -108939 | -133007 | -3182695.98 | 20 | 42 | 10 | 0 | 2 | n-Eisocane (g) --> 10 C2H4 + H2 | 233870 | 1490 | 3463 | 102 | 24379 | 258249 | 1645 | 3824 |
| 22 | 310.6 | n-Docosane (g) | -118760 | -118884 | | | 22 | 46 | 11 | 0 | 2 | n-Docosane (g) --> 11 C2H4 + H2 | 256216 | 1485 | 3451 | 115.6 | 27629 | 283845 | 1645 | 3823 |
| 24 | 338.7 | n-Tetracosane (g) | -128610 | -165920 | | | 24 | 50 | 12 | 0 | 2 | n-Tetracosane (g) --> 12 C2H4 + H2 | 278562 | 1481 | 3441 | | | | | |
| 26 | 366.7 | n-Hexacosane (g) | -138460 | SVN | | | 26 | 54 | 13 | 0 | 2 | n-Hexacosane (g) --> 13 C2H4 + H2 | 300908 | 1477 | 3433 | | | | | |
| 28 | 394.8 | n-Octacosane (g) | -148310 | SVN | | | 28 | 58 | 14 | 0 | 2 | n-Octacosane (g) --> 14 C2H4 + H2 | 323254 | 1474 | 3426 | | | | | |
| 30 | 422.8 | n-Triacontane (g) | -158160 | -79373.8 | | | 30 | 62 | 15 | 0 | 2 | n-Triacontane (g) --> 15 C2H4 + H2 | 345600 | 1471 | 3420 | 142.2 | 33987 | 379587 | 1616 | 3756 |
| 30 | 450.9 | Squalane (g) - Hexamethyltetracosane | | | -206752 | | 32 | 66 | 16 | 0 | 2 | Squalane (g) - Hexamethyltetracosane --> 16 C2H4 + H2 | | | | | | 406688 | 1624 | 3774 |
| 32 | 450.9 | n-Dotriacontane (g) | -168010 | SVN | | | 32 | 66 | 16 | 0 | 2 | n-Dotriacontane (g) --> 16 C2H4 + H2 | 367946 | 1469 | 3414 | | | | | |
| 34 | 478.9 | n-Tetratriacontane (g) | -177860 | SVN | | | 34 | 70 | 17 | 0 | 2 | n-Tetratriacontane (g) --> 17 C2H4 + H2 | 390292 | 1467 | 3410 | | | | | |
| 36 | 507.0 | n-Hexatriacontane (g) | -187710 | SVN | | | 36 | 74 | 18 | 0 | 2 | n-Hexatriacontane (g) --> 18 C2H4 + H2 | 412638 | 1465 | 3405 | | | | | |
| 38 | 535.0 | n-Octatriacontane (g) | -197560 | SVN | | | 38 | 78 | 19 | 0 | 2 | n-Octatriacontane (g) --> 19 C2H4 + H2 | 434984 | 1463 | 3402 | | | | | |
| 40 | 563.1 | n-Tetracontane (g) | -207410 | SVN | | | 40 | 82 | 20 | 0 | 2 | n-Tetracontane (g) --> 20 C2H4 + H2 | 457330 | 1462 | 3398 | 132.2 | 31597 | 488927 | 1563 | 3633 |
| | | | | | ▨ | = measured | | | | | | | | | | | | | | |
| ***Cracking of alkane to form large fragments (alkane + alkene)*** | | | | | | | | | | | | | | | | | | | | |
| 4 | 58.1 | n-Butane (g) | -30150 | SVN | | | 4 | 10 | | | | | | | | | | | | |
| 4 | 56.1 | 1-Butene (g) | -30 | SVN | | | 4 | 8 | | | | n-Octane --> n-Butane + 1-Butene | 19630 | 309 | 719 | | | | | |
| 5 | 72.2 | n-Pentane (g) | -35000 | SVN | | | 5 | 12 | | | | | | | | | | | | |
| 5 | 70.1 | 1-Pentene (g) | -5000 | SVN | | | 5 | 10 | | | | n-Decane --> n-Pentane + 1-Pentene | 19660 | 249 | 578 | | | | | |
| 6 | 84.2 | 1-Hexene (g) | -9960 | SVN | | | 6 | 12 | | | | n-Dodecane --> n-Hexane + 1-Hexene | 19590 | 207 | 481 | | | | | |
| 7 | 100.2 | n-Heptane (g) | -44885 | SVN | | | 7 | 16 | | | | | | | | | | | | |
| 7 | 98.2 | 1-Heptene (g) | -14885 | SVN | | | 7 | 14 | | | | n-Tetradecane --> n-Heptane + 1-Heptene | 19590 | 178 | 413 | | | | | |
| 8 | 112.2 | 1-Octene (g) | -19810 | SVN | | | 8 | 16 | | | | n-Hexadecane --> n-Octane + 1-Octene | 19590 | 156 | 362 | | | | | |
| 10 | 140.3 | 1-Decene (g) | -29660 | SVN | | | 10 | 20 | | | | n-Eicosane --> n-Decane + 1-Decene | 19590 | 125 | 290 | | | | | |
| 12 | 168.3 | 1-Dodecene (g) | -39510 | SVN | | | 12 | 24 | | | | n-Tetracosane --> n-Dodecane + 1-Dodecene | 19590 | 104 | 242 | | | | | |
| 14 | 196.4 | 1-Tetradecene (g) | -49360 | SVN | | | 14 | 28 | | | | n-Octacosane --> n-Tetradecane + 1-Tetradecene | 19590 | 89 | 208 | | | | | |
| 16 | 224.4 | 1-Hexadecene (g) | -59210 | SVN | | | 16 | 32 | | | | n-Dotriacontane --> n-Hexadecane + 1-Hexadecene | 19590 | 78 | 182 | | | | | |
| ***Cracking of alkene to form large alkene fragments*** | | | | | | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | 1-Dodecene -->2 1-Hexene | 19590 | 209 | 487 | | | | | |
| | | | | | | | | | | | | 1-Tetradecene -->2 1-Heptene | 19590 | 180 | 417 | | | | | |
| | | | | | | | | | | | | 1-Hexadecene -->2 1-Octene | 19590 | 157 | 365 | | | | | |
| ***Cracking of naphthene to form large alkene fragments*** | | | | | | | | | | | | | | | | | | | | |
| 6 | 84.2 | Cyclohexane (g) | -29430 | | | | 6 | 12 | | | | Cyclohexane -->2 Propylene | 39188 | 838 | 1948 | | | | | |
| 8 | 112.2 | Cyclooctane (g) | -30139 | NIST | | | 8 | 16 | | | | Cyclooctane --> 2 1-Butene | 30079 | 482 | 1121 | | | | | |
| 10 | 140.3 | Cyclodecane (g) | -36317 | NIST | | | 10 | 20 | | | | Cyclodecane -->2 1-Pentene | 26317 | 338 | 785 | | | | | |
| 12 | 168.3 | Cyclododecane (g) | -60542.5 | Chemeo - Joback | | | 12 | 24 | | | | Cyclododecane -->2 1-Hexene | 40623 | 434 | 1010 | | | | | |
| 14 | 196.4 | Cyclotetradecane (g) | -57170.2 | NIST | | | 14 | 28 | | | | Cyclotetradecane -->2 1-Heptene | 27400 | 251 | 584 | | | | | |
| 16 | 224.4 | Cyclohexadecane (g) | -86164 | Chemeo - Joback | | | 16 | 32 | | | | Cyclohexadecane -->2 1-Octene | 46544 | 373 | 868 | | | | | |
| ***Cracking of naphthene to form ethylene*** | | | | | | | | | | | | | | | | | | | | |
| 10 | 140.3 | Cyclodecane (g) | -36317 | NIST | | | 10 | 20 | 5 | 0 | 0 | Cyclodecane (g) --> 5 C2H4 | 98797 | 1268 | 2947 | | | | | |
| 12 | 168.3 | Cyclododecane (g) | -60542.5 | Chemeo - Questionable value | | | 12 | 24 | 6 | 0 | 0 | Cyclododecane (g) --> 6 C2H4 | 135519 | 1449 | 3369 | | | | | |
| 14 | 196.4 | Cyclotetradecane (g) | -57170.2 | NIST | | | 14 | 28 | 7 | 0 | 0 | Cyclotetradecane (g) --> 7 C2H4 | 144642 | 1326 | 3082 | | | | | |
| 16 | 224.4 | Cyclohexadecane (g) | -86164 | Chemeo - Joback | | | 16 | 32 | 8 | 0 | 0 | Cyclohexadecane (g) --> 8 C2H4 | 186132 | 1493 | 3470 | | | | | |
| ***Dealkylation of alkylbenzene to form benzene + alkene*** | | | | | | | | | | | | | | | | | | | | |
| 6 | 78.1 | Benzene (g) | 19820 | SVN | | | 6 | 6 | | | | | | | | | | | | |
| 9 | 120.2 | n-Propyl benzene (g) | 1869 | NIST | | | 9 | 12 | | | | n-Propyl benzene (g) --> Benzene (g) + Propylene (g) | 22830 | 342 | 795 | | | | | |
| 10 | 128.2 | Naphthalene (g) | 35851 | NIST | | | 10 | 8 | | | | | | | | | | | | |
| 13 | 170.3 | n-Propyl naphthalene (g) | 24971 | Chemeo - Joback | | | 13 | 14 | | | | n-Propyl naphthalene (g) --> Naphthalene (g) + Propylene (g) | 15759 | 167 | 387 | | | | | |
| 14 | 184.3 | n-Butyl naphthalene (g) | 20038 | Chemeo - Joback | | | 14 | 16 | | | | n-Butyl naphthalene (g) --> Naphthalene (g) + 1-Butene (g) | 15783 | 154 | 358 | | | | | |