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**IMPROVED METHOD FOR THE
MEASUREMENT OF FULL AND PARTIAL
HEAT OF VAPORIZATION OF GASOLINE
AND ETHANOL/GASOLINE BLENDS**

Executive Summary

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COORDINATING RESEARCH COUNCIL, INC.
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To: CRC AVFL-27-2 Committee

From: Gina M. Fioroni

Date: September 10, 2020

Re: Executive Summary: Improved Method for the Measurement of Full and Partial Heat of Vaporization of Gasoline and Ethanol/Gasoline Blends

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The Heat of Vaporization (HOV) is a measure of the amount of energy required to transform a liquid substance into a gas. HOV is an important fuel property that can help enable higher compression-ratio direct injection engines by providing a cooling effect that can effectively increase fuel knock resistance. Methods to directly measure this fuel property in complex gasoline samples are not well developed. The objective of this study was to further develop a method to measure the total and partial HOV by acquiring three replicate measurements of the HOV of ten market gasolines. The market gasoline samples were chosen to have a wide range of properties to assess the method’s capability across the entire volatility range with an emphasis on understanding how well the method captures the initial 10 percent (%) of sample evaporation. A Differential Scanning Calorimeter coupled to a Thermogravimetric Analysis (DSC/TGA) was used to take triplicate measurements in randomized order at three different target temperatures: room temperature (16°C-25°C), 10°C, and 0°C. The experimental total HOV results from the DSC/TGA were compared to those calculated from a Detailed Hydrocarbon Analysis (DHA).

The project was separated into three main tasks. Task 1 simply involved sample receipt and proper storage of all the gasoline samples. In task 2, two summer E10 (10% by volume ethanol) market gasoline fuels and Fuels for Advanced Combustion Engines (FACE) gasoline G were supplied to the National Renewable Energy Laboratory (NREL) from the Coordinating Research Council (CRC) – FACE G was blended with ethanol at 30 volume %. Task 2 focused on the ability of the DSC/TGA method to measure the total HOV, which was compared to the HOV from DHA. Randomized, triplicate measurements were run under ambient room temperature conditions (uncontrolled, 16°C-25° C) with an effort to capture the initial 10% of sample evaporation. Results are shown in Table 1.

Table 1. Task 2 Total HOV by DSC/TGA and DHA (room temperature, 16°C-25°C)

NREL ID	Sample ID	DHA (kJ/kg)	DSC/TGA Replicate 1 (kJ/kg)	DSC/TGA Replicate 2 (kJ/kg)	DSC/TGA Replicate 3 (kJ/kg)	Average (kJ/kg)	Std. Dev.	% RSD	% Difference from DHA
2231480	Summer 1 (E10)	405	426	406	394	408	16.2	4	0.9
2219920	Summer 2 (E10)	412	389	385	416	397	17	4.3	-3.7
2219921	FACE G (E30)	526	537	517	501	518	18	3.5	-1.4

Task 2 demonstrated that the DSC/TGA instrument (with modifications to disable the door closing mechanism) was able to capture the initial sample evaporation with approximately 5% sample loss for highly volatile samples (winter gasolines with higher vapor pressure) at room temperature. Comparison of the total HOV between experimental measurement and that calculated by DHA showed excellent agreement with results that were less than 5% different. Triplicate analysis also demonstrated excellent repeatability, with results within 5% relative standard deviation (% RSD).

For task 3, six winter market gasolines and four summer market gasolines with a wide range of properties were supplied to NREL. All samples were E10, except one sample which was an E0. Under Task 3, NREL measured the total HOV as well as the partial HOV (at intervals of 10% of sample evaporated) at three target temperatures of room temperature, 10°C, and 0°C. To achieve the two lower temperatures the DSC/TGA apparatus was placed in a cold chamber developed specifically for this project. For room temperature conditions, no temperature control was utilized, while temperatures of 10°C and 5°C were obtained by building a cold chamber that housed the analytical instrument. The 0°C target temperature could not be achieved with the cold chamber, however a temperature of nominally 5°C was achieved and used as the low temperature point. A pan with a lid was used under ambient conditions to avoid an unacceptably rapid evaporation rate. It was not practical to use a lid in the cold chamber experiments, due to the ergonomics of placing the lid on the pan which would have taken several seconds, however, evaporation rates were lower because of the lower temperatures, making use of the lid less of a necessity. The analysis was performed in triplicate for a total of 90 sample runs. The total HOV at the three temperatures was also calculated by DHA for comparison and results are shown in Table 2.

Several important outcomes were drawn from Task 3 results (Table 2). Comparison of the total HOV between the DSC/TGA and DHA again showed excellent agreement at all three temperatures, with those at 10°C and 5°C being more consistent – results were within 10% RSD except for a handful of cases. For partial HOV measurements (Table 3), results under room temperature conditions were highly variable, especially for the first 20-30% of sample evaporated. In addition, two of the summer gasoline samples (summer gasolines 3 and 4) did not fully evaporate when utilizing the lid at room temperature. To accommodate for this, repeat measurements were made with no lid.

Table 2: Task 3 Total HOV by DSC/TGA and DHA at room temperature (16°C-25°C), 10°C, and 0°C

NREL ID	ID	HOV DSC/TGA (kJ/kg)			HOV DHA (kJ/kg)			% Difference		
		16°C-25°C	10°C	5°C	16°C-25°C	10°C	5°C	16°C-25°C	10°C	5°C
199043	Winter 1 (E10)	362	417	417	417	424	428	14.1	1.7	2.6
199039	Winter 2 (E10)	373	396	407	420	427	431	11.9	7.5	5.7
199044	Winter 3 (E10)	351	405	395	410	417	420	15.5	2.9	6.1
199042	Winter 4 (E10)	440	400	431	420	427	431	-4.7	6.5	0.0

199041	Winter 5 (E10)	417	388	407	419	426	430	0.5	9.3	5.5
199040	Winter 6 (E10)	370	382	419	408	414	418	9.8	8.0	-0.2
213629	Summer 1 (E10)	385	400	404	423	430	434	9.4	7.2	7.2
213627	Summer 2 (E10)	398	403	393	420	427	430	5.4	5.8	9.0
205266	Summer 3 (E10)	416*	405	386	417	424	427	0.2	4.6	10.1
219267	Summer 4 (E0)	356*	349	338	359	365	368	0.8	4.5	8.5

* Results from experiment with no lid

Table 3: Task 3 Partial HOV by DSC/TGA at room temperature (16°C-25°C), 10°C, and 0°C

Measured Heat of Vaporization (kJ/kg)*										
% of Sample Evaporated	Winter #1	Winter #2	Winter #3	Winter #4	Winter #5	Winter #6	Summer #1	Summer #2	Summer #3	Summer #4
Room Temperature										
10%	421	448	441	360	415	373	371	371	202	173
20%	449	465	464	393	438	415	406	406	269	226
30%	468	476	478	420	457	447	433	433	325	271
40%	480	482	484	441	469	467	453	453	371	309
50%	482	482	481	457	476	476	465	465	406	338
60%	477	477	471	466	477	474	469	469	430	358
70%	463	466	452	470	472	461	465	465	443	371
80%	441	449	424	469	462	436	453	453	446	376
90%	410	427	388	461	446	401	434	434	438	373
100%	372	399	344	448	425	354	407	407	419	361
10°C										
10%	184	145	166	133	194	203	200	200	214	191
20%	246	224	235	208	264	268	261	261	271	234
30%	298	290	294	271	322	321	313	313	319	271
40%	342	344	342	323	368	363	354	354	358	301
50%	376	385	380	364	402	394	386	386	388	326
60%	402	413	406	394	424	414	408	408	410	343
70%	418	428	422	413	434	422	421	421	423	355
80%	426	430	427	421	431	419	424	424	427	361
90%	424	419	421	417	417	405	418	418	422	360
100%	414	396	404	402	390	379	401	401	409	353
0°C										

10%	183	189	177	170	201	238	224	224	202	198
20%	257	259	245	234	265	294	282	282	259	233
30%	319	317	303	289	319	341	330	330	307	263
40%	369	364	349	335	362	379	368	368	346	289
50%	407	400	384	373	396	407	397	397	376	310
60%	434	424	408	402	418	427	415	415	396	326
70%	448	437	422	423	431	437	424	424	408	338
80%	450	439	424	434	433	439	423	423	410	346
90%	440	429	415	437	425	431	413	413	403	348
100%	418	408	396	431	407	414	392	392	387	346

***Results are an average of 3 runs at each temperature**

One of the most valuable conclusions was that the lower temperature experiments at 10°C and 5°C enabled more reproducible measurements for both total and partial HOV. This result could be due to a couple of reasons. First, the temperature control in the cold chamber was much more consistent than the laboratory room temperature control. Additionally, cold chamber experiments, due to ergonomic challenges within the cold chamber, did not allow for the use of a lid on the sample pan. The reproducibility of the evaporation rate as well as the repeatability of the experiment is impaired by inconsistent pan/lid fit. The combination of colder temperature (slowing the evaporation rate) and lack of a pan lid (accelerating evaporation rate) yielded acceptable evaporation rates that were more repeatable than those at room temperature. This suggests that future experiments seeking high precision (repeatability and reproducibility) should be run in a cold chamber with no lid on the sample pan.

In summary, overall, the DSC/TGA and DHA both provide reliable methods for total HOV results for market gasoline samples. The percent difference between the two methods was generally 5% or less, especially for the 10°C and 5°C measurements where there was better temperature control during the experiment and variation due to the pan/lid fit was eliminated. Using a lid on top of the pan for room temperature conditions reduced sample evaporation prior to initiating the experiment, such that sample loss was limited to approximately 5%, however, this also resulted in difficulty fully evaporating two of the gasoline samples. Repeatability between replicates was excellent with the %RSD being 10% or less except in a handful of cases which were mostly at room temperature conditions. Running experiments in the temperature-controlled chamber at 10°C utilizing a pan with no lid appeared to be the most reliable method for experimentally determining the total HOV by DSC/TGA.

As with the total HOV results, the most reliable partial HOV measurements were obtained at 10°C or 5°C using a sample pan with no lid to avoid the highly variable results due to the pan/lid fit. Future experiments run with no lid under tight temperature control will yield the most reproducible and accurate results.