
**Committee of Experts on the Transport of Dangerous Goods
and on the Globally Harmonized System of Classification
and Labelling of Chemicals**

4 December 2015

**Sub-Committee of Experts on the Transport
of Dangerous Goods**

Forty-eighth session

Geneva, 30 November – 9 December 2015

Item 3 of the provisional agenda

Listing, classification and packing

**Sub-Committee of Experts on the Globally
Harmonized System of Classification and
Labelling of Chemicals**

Thirtieth session

Geneva, 9 – 11 December 2015

Item 2 of the provisional agenda

**Joint work with the Sub-Committee of
Experts on the Transport of Dangerous
Goods (TDG Sub-Committee)**

Crude oil – classification and transport issues

Transmitted by the expert from Canada

Purpose

1. Following ST/SG/AC.10/C.3/2014/49, to debrief the UN Sub-Committee of Experts on the Transportation of Dangerous Goods (UNSCETDG) and the UN Sub-Committee on the Globally Harmonized System of Classification and Labelling of Chemicals (UNSCEGHS) on the findings from a focused sampling and testing study to assess the composition and properties of crude oils transported by road and rail in Canada.

Background and Introduction

2. North America has experienced a significant increase in crude oil supply, bolstered both by growing production in the Canadian oil sands and the recent expansion of shale oil and natural gas production in the United States of America and Canada.

3. North American shale oil has been mostly in geographic areas not linked to traditional crude oil or natural gas pipelines, resulting in an increase in surface transport. Surface (road and rail) transport has also enabled crude transport to different refinery capacities situated across North America. This crude oil is known to contain significantly more volatile components than what has been traditionally transported as UN 1267.

4. This exponential increase in surface movement of crude oil has led authorities within Canada and the United States of America to carefully consider transport safety impacts as well as potential impacts to the environment. These efforts have been prioritized based on a series of major accidents across North America involving crude oil transport by rail – including a catastrophic incident that caused numerous fatalities and destroyed much of Lac Mégantic, Quebec, in July 2013.

5. The objective of the Canadian study was to verify the application of current classification requirements as described in the UN Model Regulations for Class 3, Flammable liquids, and Class 2, Gases.

6. In total, 68 samples of crude oil destined for transport by rail or road in Canada, representing a wide range of crude oils, were collected and analysed. Some samples were taken under pressure to maintain their most volatile components, whilst others were taken at atmospheric pressure for tests that do not require pressurised, sealed samples, or when the crude oil was too viscous to sample under pressure.

7. The samples were tested to determine properties including, but not limited to, Initial Boiling Point (IBP), Reid Vapor Pressure (RVP), True Vapor Pressure (TVP), compositional analysis, hydrogen sulphide (H₂S) analysis in the vapor phase and flammability testing of the vapor phase. A complete list of properties and test methods can be found in Annex A.

Results and Discussion

Vapour Pressure

8. Vapour pressure is a key property in determining whether a substance meets the definition of a liquid or gas as per the UN classification criteria.

9. The UN Model Regulations define a liquid in Chapter 1.2:

a. Liquid: means a dangerous good which at 50°C have a vapour pressure of not more than 300 kPa (3 bar), which is not completely gaseous at 20°C and at a pressure of 101.3 kPa, and which has a melting point or initial melting point of 20°C or less at a pressure of 101.3 kPa. A viscous substance for which a specific melting point cannot be determined shall be subjected to the ASTM D 4359-90 test; or to the test for determining fluidity (penetrometer test) prescribed in section 2.3.4 of Annex A of the European Agreement concerning the International Carriage of Dangerous Goods by Road (ADR);

10. The UN Model Regulations define a gas in Chapter 2.2:

2.2.1.1 *A gas is a substance which:*

(a) At 50 °C has a vapour pressure greater than 300 kPa; or

(b) Is completely gaseous at 20 °C at a standard pressure of 101.3 kPa.

11. True Vapor Pressure (TVP)¹ is explained as the vapor pressure exerted by both the liquid crude oil and the gases contained within, at a specific temperature and vapor/liquid (V/L) ratio.

12. Reid Vapor Pressure (RVP)² is explained as the vapor pressure exerted by the liquid crude oil at a V/L of 4:1 at 37.8 °C.

13. Vapour pressures found using the TVP testing method indicated that most of the crude oils sampled would boil at the testing temperature of 50 °C if those crude oils were exposed to the atmosphere (their TVP is greater than 101.3 kPa at 50 °C).

¹ True Vapor Pressure (TVP): a term used to describe the pressure exerted by a fluid at a very low vapor/liquid ratio at a specified temperature; empirically, a result to represent the bubble point, defined as a zero vapor/liquid (V/L) ratio up to say 0.02 V/L ratio (lower limit of test methods such as ASTM D6377). Source: <http://goo.gl/0cDck5>

² Reid Vapor Pressure (RVP): a term commonly defined by ASTM D323 Reid Vapor Pressure Method - used to describe the pressure exerted by an air saturated fluid at a vapor/liquid ratio of 4:1 at 37.8°C. Source: <http://goo.gl/0cDck5>

14. One sample collected met the definition of a Class 2.1 – Flammable Gas based on its vapour pressure and flammability test results.

15. The TVP values obtained are higher than the RVP values for the crude oil samples tested by both methods. During a TVP test, the volatile components stay in the sample during both sampling and the analysis and contribute to the pressure reading. This is not the case for a RVP test: both sampling and handling generally allow the volatile components to escape; their hazards are not captured during testing but are present in transport.

Initial Boiling Point

16. IBP analysis is used in determination of packing groups for the transport of Class 3 – Flammable Liquids. Section 2.3.2.6 of the UN Model Regulations links flash point and IBP for the hazard grouping and packing group assignment.

17. Section 2.3.4 of the UN Model Regulations lists ASTM D86-07a as a method for determination of IBP for petroleum products at atmospheric pressure. Industry has commonly used this method, however this is problematic as the method is open to the atmosphere – volatile light ends are not maintained during testing in an open cup method. As well, its physical limitation will not capture light ends that escape during the IBP determination, rendering the method incapable of determining IBP values at or below 0 °C due to the use of a water cooled condenser. As a result, this method is incapable of resolving the IBP contributions of components such as methane, ethane, propane, etc. in crude oil and other products where this method may be used.

18. Canada identified alternate methods, not currently listed in the UN Model Regulations, that would be more appropriate to crude oils such as those recovered as part of this study. Analysis by injection using ASTM D8003 or ASTM D7169 allows for the injection of pressurised samples into the analysis instrument, avoiding the loss of highly volatile components and maintaining sample integrity. ASTM D8003 was used for the light ends determination (C1 to nC9) and coupled with ASTM D7169 for C9 to C100 determination.

19. IBP analysis on sealed, pressurised samples using composition data by ASTM D8003 / ASTM D7169 of crude oil samples resulted in consistently lower boiling point readings than results obtained by ASTM D86, for those samples tested by both methods. The average difference was 46.3 °C when comparing samples that had the highest proportion of light ends. The IBP is the temperature at which 0.5 weight percent of the sample has eluted, as defined in ASTM D7169 and American Petroleum Institute (API) Recommended Practice 3000.

20. IBP determined by ASTM D86 resulted in several crude oil samples being assigned PG II, whereas the ASTM D8003 / ASTM D7169 data for those same samples resulted in PG I assignment. Using IBP criteria, 56 of the 68 samples belonged in Packing Group I, the highest hazard group for Class 3 – Flammable Liquids.

21. The table below summarises differences between IBP determinations made using ASTM D86 and the ASTM D8003 / ASTM D7169 methods:

Sample Type	Average IBP (°C), ASTM D86	Average IBP (°C), ASTM D8003 / ASTM D7169	Average Δ (°C)
Light Oil	35.3	-17.9	53.2
Medium Oil	92.8 (one point only)	5.8	87.0
Diluted Heavy Oil	30.9	-6.2	37.1
Synthetic Crude	35.8	-0.6	36.4
Diluted Bitumen	32.9	-0.6	33.5
Synthetic Bitumen	52.8	-0.6	53.4
Condensate	29.3	-11.4	40.7

Hydrogen sulphide (H₂S)

22. Hydrogen sulphide is a highly toxic gas normally found in varying amounts in crude oil. In Canada, the Occupational Safety and Health (OSH) exposure limit is defined as 20 ppm. The immediately dangerous to health and life limit (IDLH) is defined as 100 ppm. At 500-1000 ppm, death is imminent or immediate.

23. H₂S content in petroleum crude oil is a known hazard when handling and transporting crude oil. While crude oil is commonly considered a liquid, the H₂S hazard exists in the vapour space above crude oil in a means of containment, or can be present in an emergency situation when crude oil is exposed to the atmosphere and H₂S is allowed to evolve out of solution.

24. Vapour phase measurement of H₂S taken from Canadian crude oil samples ranged from 0-65000 ppm, 26 of the 68 samples collected crude oil samples registered values above 1000 ppm. Of these, 20 samples ranged from 1000 ppm to 20 000 ppm, and 6 samples ranged from 24 000 ppm to 65 000 ppm. It should be noted that testing for H₂S is conducted at 60 °C as per the test method; for crude oils that were too volatile (e.g., condensate), the tests were conducted at ambient temperature to avoid the loss of material.

25. The levels of H₂S found in some crude oil samples are significantly higher than the threshold limit value of the OSH standard. In an accident scenario, or during regular transport operations and handling/transferring, these high H₂S crude oils may pose a significant risk to persons handling the crude oil.

26. It should be noted the test results collected have a +/- 25% accuracy, the testing method has a large margin of error but is still indicative of the magnitude and approximate hazard posed by the H₂S present in crude oil.

Considerations

27. Elevated vapor pressures of crude oil may require classification as a Class 2 – Gas, and may affect selection of means of containment. A crude oil that meets the definition for Class 2.1 – Flammable Gas designation requires a more robust means of containment during transport (pressure tank car or highway tank).

28. The use of pressurised sampling and testing for crude oil is an important factor. The hazard posed by dissolved light ends cannot be accurately captured by atmospheric sampling and testing which may lead to erroneous data used for classification purposes.

29. The limitations of ASTM D5705 for testing H₂S point to a need to develop a method of measuring H₂S in the vapour phase that is fit for purpose and has the capability of controlling the variables affecting release of H₂S (sampling method, temperature, V/L ratio and agitation). Measuring vapour phase H₂S using proper sampling techniques, and temperature and headspace conditions in the range normally encountered during operations or transport, would give a better assessment of the hazard. Give this, Canada is participating in an industry-led research and development project to develop test standards for H₂S analysis.

30. Development of a method and knowledge of H₂S concentrations in the vapour phase would help to inform regulators and provide guidance on setting thresholds for H₂S. Testing conditions could then be specified in regulations. Canada is currently advancing research in this area and welcomes any data or input from interested parties of the UNSCETDG.

Conclusion

31. Canada wishes to share the above mentioned data with both the UNSCETDG and UNSCEGHS for consideration. Events over the last few years in North America have caused Canada to focus research efforts on the classification of crude oil. The results obtained in this first phase of testing is of relevance to all members of the UNSCETDG and UNSCEGHS where crude oil is extracted, transported, or handled.

32. Canada will continue sharing research results as they are available with both the UNSCETDG and UNSCEGHS. A copy of the research results is attached in Annex B.

Annex A – Test Methods Used

Test Method	Title
APHA4500 S2-E	Sulphur in Water, Extractable (Methylene Blue Auto-Colourimetry) Output: concentration of H ₂ S in solution, mg/L Detection Limit: 0.002mg/L
ASTM D56	Standard Test Method for Flash Point by Tag Closed Cup Tester Output: flash point, °C
ASTM D86	Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure, Initial Boiling Point Output: initial boiling point (IBP), °C
ASTM D93	Standard Test Methods for Flash Point by Pensky-Martens Closed Cup Tester Output: flash point, °C
ASTM D323M	Standard Test Method for Vapor Pressure of Petroleum Products (Reid Method), Modified. Output: vapour pressure at V/L 4:1 and 50°C, °C
ASTM D3828	Standard Test Methods for Flash Point by Small Scale Closed Cup Tester Output: flash point, °C
ASTM D4007	Water and Sediment in Crude Oil by the Centrifuge Method (Laboratory Procedure) Output: water content, volume %
ASTM D5002	Standard Test Method for Density and Relative Density of Crude Oils by Digital Density Analyzer Output: density, kg/m ³
ASTM D5705	Measurement of Hydrogen Sulphide in the Vapor Phase Above Residual Oils Output: concentration of H ₂ S in the vapour phase, ppm
ASTM D6377	Standard Test Method for Determination of Vapor Pressure of Crude Oil: VPCR _x (Expansion Method) Output: vapour pressure at V/L 0.2:1 and 50°C, kPa
ASTM D7169	Standard Test Method for Boiling Point Distribution of Samples with Residues Such as Crude Oils and Atmospheric and Vacuum Residues by High Temperature Gas Chromatography Output: boiling point distribution, mass %
ASTM D7678	Total Petroleum Hydrocarbons (TPH) in Water and Wastewater Solvent Extraction using Mid-IR Laser Spectroscopy Output: concentration of TPH in water, mg/L (ppm)

Test Method	Title
ASTM D7900	Standard Test Method for Determination of Light Hydrocarbons in Stabilized Crude Oils by Gas Chromatography Output: light end composition, mass %
GOR/GC	Atmospheric Flash of Hydrocarbon Samples for Gas-Oil Ratio Determination (GOR) Determination and Gas Composition by GC Output: GOR, m3/m3 and flashed gas composition, mass %
ASTM D8003	Standard Test Method for Determination of Light Hydrocarbons and Hydrocarbon Boiling Point Distribution and Cut Point Intervals in Live Crude Oils and Condensates via Gas Chromatography Output: light end composition, mass %
ISO 10156	Gases and gas mixtures – Determination of fire potential and oxidizing ability for the selection of cylinder valve outlets Output: flammability range with air, % of gas in air

ANNEX B – AITF Report

See INF.62/Add.1