PREVENTION OF AIR POLLUTION FROM SHIPS

The Physical Behaviour of Crude Oil influencing its Carriage by Sea (CRUCOGSA) and subsequent projects

Submitted by INTERTANKO

SUMMARY

Executive summary: This information paper provides a brief report on a number of industry studies carried out over the last few years. The paper presents the objectives and the results of these Studies, mainly aimed to obtain better knowledge of the physical properties of crude oils and develop new operational procedures for a more efficient transportation of crude oil by sea as well as the limitation of maritime pollution from crude oils.

Action to be taken: Paragraph 10

Related documents: MEPC 46/23 (page 53 paragraph 10.15), BLG 3/10/2 and MEPC 43/21 (annex 12)

The three-year research programme entitled The Physical Behaviour of Crude Oil influencing its Carriage by Sea (CRUCOGSA) was co-sponsored by INTERTANKO, B.P. Oil, B.P. Shipping, Chevron International, Exxon International, the U.K. Maritime and Coastguard Agency (MCA), Gotaas Larsen/Osprey, Petrofina Marine, Repsol, Agip Petroli, Mobil, Sun Oil, Arco and The Norwegian Maritime Directorate.

The purpose and the objectives of CRUCOGSA were:

1. To compile a database of information for the behaviour of crude oil during its transportation by sea.

2. To supply data in a user friendly form for vessels’ officers to use when handling and transporting crude oil.

3. To investigate the causes or reasons for identified operational difficulties (e.g. pumping, COW and gas emissions). This will include the supply of mathematical models to predict the required temperature in order to avoid precipitation of sludge or for attaining a more efficient washing temperature/programme for
closed cycle crude oil washing and, to aid tanker operators with sludge minimisation and conversely with the minimisation of vapour loss from heating.

.4 To supply data that might assist with the modification of current international Regulations where they are believed to be inappropriate for vessel guidance or use.

3 The following results have been achieved so far:

.1 CRUCOGSA has established a comprehensive database of 73 crude oils. This is of a lesser size than originally contemplated but still represents a good cross section of crude oils currently carried by sea and is the best of its kind.

.2 INTERTANKO has already begun to provide officers onboard tankers advice for more efficient and environmentally sound cargo operations. In addition, the database and the study results were made available to all INTERTANKO Members and to many others.

.3 INTERTANKO has developed new operational procedures and some further procedures are currently under development.

.4 INTERTANKO has already suggested and MEPC 43/21 (Annex 12) approved amendments to Section 9 of IMO Manual on Crude Oil Washing. Other submissions are under consideration.

4 CRUCOGSA Study has determined the physical behaviour of a variety of crude oils whilst being transported such that increased efficiency can be obtained by the industry for controlling of volumetric loss from this diminishing resource.

5 Knowledge of the physico-chemical behaviour of crude oil being carried aboard a tanker will not only have a significant impact upon the efficient carriage of oils and oil loss control but also will supply data to the general maritime industry for assistance in pollution control from tankers. Some of the criteria investigated are of significant value in the assessment of oil spill response methods in the event of an oil spill and the prediction of the behaviour and fate of an oil slick. This has been materialised by the supply of relevant information from INTERTANKO to ITOPF to update their data system and files.

6 Currently, when tankers are carrying certain crude oils unheated under certain environmental conditions tank sludging is not uncommon. Such occurrences are fairly regular during the northern hemisphere winter months and cause exaggerated overall losses during the overall transportation of cargoes. Likewise, when transporting volatile crude cargoes under certain environmental conditions there are significant Volatile Organic Compound (VOC) emissions from cargo tanks. The ultimate objectives as follow up action from the CRUCOGSA research is to define temperature criteria enabling the tanker officers to keep a crude oil cargo in its liquid phase during its transportation at sea.

7 As a first follow up action, INTERTANKO has initiated a new study entitled Vapour Emission Study (VOCON), with the aim of assessing the extent of these emissions and develop an operational measure to limit the Volatile Organic Compound (VOC) Emissions from crude carriers cargo tanks during transportation. A copy of a developed method - the INTERTANKO VOCON Operational Procedure - is provided in annex 2.
8 Annex 1 of this paper gives a brief Report of the CRUCOGSA Study. Annex 2 presents the INTERTANKO VOCON Operational Procedure for limitation of VOC emissions during transportation of crude oils.

9 Pending on the agreement of the IMO Secretariat, INTERTANKO will also make a presentation during the MEPC 47th Session for the benefit of delegates so as to be better informed on the content of this research programme and further activities developed there from.

**Action requested of the Committee**

10 INTERTANKO invites the Committee to note these ongoing studies as part of the tanker industry’s strategy for protection of tanker crews, for safer cargo operation and a self-regulatory attempt to limit cargo losses.
ANNEX 1

The Physical Behaviour of Crude Oil during Transportation and its impact upon the Carriage of Crude Oil by Sea with particular regard to Emissions of Volatile Organic Compounds (VOC)

The Physical Behaviour of Crude Oil Influencing its Carriage by Sea – CRUCOGSA

This three year research project, undertaken between 1996 and 1999, forms the first stage of a larger research programme entitled The Marine Transportation of Crude Oil (MATCO). The project, due to its importance and potential findings/impact, was sponsored by a true cross section of the Crude Oil transportation industry and interested bodies ranging from INTERTANKO to a variety of Oil Companies, Government Organisations and individual oil company and independent tanker fleets.

1 Background and Objectives of the Research

The general objectives or goals for the CRUCOGSA project were, from its inception, to determine the physical behaviour of a variety of crude oils whilst being transported such that increased efficiency could be obtained for industry by controlling volumetric loss of this diminishing resource. The project would also supply data that would aid in the control of liquid and vapour pollution to the environment. This, it was deemed, could create significant economic benefit to the oil industry.

The rapid increase in Crude oil value in the 1970's and again in 2000 has made industry more conscious of crude oil cargo losses. It is recognised by the industry, who are both environmentally and fiscally aware, that close monitoring and measurement of this vital feed stock source is important. Previous statistical studies, supplied some reliable overall guidance to the industry regarding volumetric loss expectation, but also derived some broad distributions for the data populations. Only limited data from the few scientific studies undertaken by the industry have been published regarding the physical behaviour of crude oils carried by sea. Where such studies have been undertaken they were restricted to a specific crude oil, type of vessel or voyage.

Knowledge of the behaviour of crude oil being carried aboard a tanker would not only have a significant impact upon the efficient carriage of oils and oil loss control but also supply data to the general maritime industry for assistance in pollution control from tankers. Some of the criteria investigated (e.g. viscosity of diverse crude oils at a variety of temperatures) would be of significant value in the decision making for appropriate oil spill response methods in the event of an oil spill and the prediction of the behaviour and fate of an oil slick.

Further, when tankers are carrying certain crude oils unheated under certain environmental conditions, tank sludging does occur. Such circumstances can occur during the northern hemisphere winter months and cause exaggerated overall losses during the overall period of transportation of cargoes. Likewise with vapour emissions, the previously reported loss of vapour, at about 0.17% of cargo volume, seemed to underestimate preliminary measurements obtained by a pilot study for this research programme of between 0.4 and 0.6% for a volatile type of crude oil.
With such ongoing, environmental consequences, monetary losses and the associated significant costs in the subsequent removal of these deposits and cleaning of vessels, more efficient transportation criteria and guidelines must be made available to those onboard tanker vessels for operational decision making. Clearly these initial and generalised goals were poorly defined for the purposes of completing a research project, notwithstanding the fact that the general objectives of the research project were clear. The project’s goals could not have been more closely defined before adequate preliminary evidence was available, given the basis of only a short preliminary pilot study, before the commencement of the main programme.

In the event and at a meeting in October 1997 the following objectives of the programme were defined and subsequently accepted by the Research Review Committee (being representatives from all the sponsoring entities) as objectives that could be achievable from the programme. The objectives became:

.1 To compile a database of information that can be reliably accessed to gain information concerning the behaviour of crude oil during its transportation by sea.

.2 To supply data in a user friendly form for vessels’ officers to use when handling and transporting crude oil.

.3 To investigate the causes or reasons for identified operational difficulties (e.g. pumping, COW and vapour emissions). This will include the supply of mathematical models to predict the required temperature in order to avoid precipitation of sludge or attaining a more efficient washing temperature/programme for closed cycle crude oil washing and, to aid tanker operators with sludge minimisation and conversely with the minimisation of vapour loss from over heating.

.4 To supply data that will assist with the modification of current international regulations where they are believed to be inappropriate for vessel guidance or use.

All of the foregoing were achieved by the research project either in full or part. Due to the extensive amount of data both of crude oil properties together with the voyage cargo and environmental records, further projects are being currently undertaken within the MATCO programme to utilise and explore the diverse permutations and combinations of information. These current projects concern both “Vapour Emission Control” (VOCON) and “Crude Oil Measurement Control” (CRUMEECON). In addition other projects have been undertaken using this scope of information, which include “Abnormal Corrosion to Crude Oil Cargo Tanks” (CRUCOR), or are under planning, “Effective Crude Oil Washing” (CRUCLEAN).

This paper will briefly address some of the overall findings from the CRUCOGSA project under the titles of the three differing phases that can be found in a crude oil cargo; namely, Vapour, Liquid and Sludges and provide interim indications obtained from both VOCON and CRUMEECON.
1.1 Current Parameters used for Crude Oil Operations

However, before continuing it is necessary to supply a broad outline of the physical parameters that are used today in operational decision making that impact the efficiency of Crude Oil tanker cargo operations and the transportation of this material.

Volatility of Crude Oil

Clearly, the extent of the volatility parameter will impact both the efficiency and effectiveness of pumping and discharge of cargo (NPSH criterion) and the pressure build up in the cargo tanks during the voyage necessitating release to the atmosphere of volatile organic compounds (VOC). The physical parameter currently used and available for guidance in decision making for these consequences is that of the cargo’s Reid Vapour Pressure. This parameter measures the volatility of the crude oil as a pressure at a liquid/vapour temperature of 100 degs F (37.8 degs C) with a liquid to vapour ratio of 1:4.

Liquid Phase Physical Parameters

The two main parameters mainly referred to are those of, Density (at 15 degs C) or its equivalent parameters – Relative Density or API Gravity recorded at 60 degs F – and, the oil’s Kinematic Viscosity at a single defined temperature – typically 40 degs C. These parameters are important to a vessel for the quantification of its cargo and assessing the required cargo temperature to render the cargo in a pumpable state.

Sludge Generating Parameters

The primary parameter available to a vessel’s command today for advices is that of the crude oil’s Pour Point temperature. This parameter is said to record the temperature at which the crude oil, once cooled, is just capable of flow or “being poured”. Thus the common understanding is that the obverse of this parameter is a rough indication as to when the crude oil will solidify to a sludge form in the cargo tanks.

2 Some Statistics for the Database Content

Number of diverse types of Samples Received from differing stages of the voyages: 2024

Number of differing Crude Oil types analysed: 73

Number of Vessels taking part of differing categories: 24

Number of Crude Oil Voyages: 361 (there were many voyages with two or more grades of crude oil onboard the vessels)

In addition to the analytical data to be obtained from the samples received the Database also records the following cargo and environmental information received from the participating vessels.
2.1 Vessel Cargo and Environmental Data Record

<table>
<thead>
<tr>
<th>Data Type or Description</th>
<th>Frequency of Reporting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cargo Tanks’ temperature, Top Middle and Bottom</td>
<td>Daily</td>
</tr>
<tr>
<td>Sea Water Temperature</td>
<td>Daily</td>
</tr>
<tr>
<td>Air Temperature</td>
<td>Every four hours</td>
</tr>
<tr>
<td>Inert Gas Line Pressure</td>
<td>Every four hours</td>
</tr>
<tr>
<td>Vessel Rolling/Pitching code</td>
<td>Every four hours</td>
</tr>
<tr>
<td>Vapour pressure release or Top Up data</td>
<td>As occurring</td>
</tr>
<tr>
<td>Wind Speed, Sea State and Vessel Course</td>
<td>Every four hours</td>
</tr>
</tbody>
</table>

In order to assess the impact of the crude oils’ behaviour during the voyage the following cargo records are also recorded within the Database for each crude oil and voyage.

2.2 Vessel Cargo Record Data

.1 Onboard Quantity (O.B.Q.) Report and Slop Tank/s quantities before loading
.2 Vessel’s cargo calculation upon completion of loading
.3 Vessel’s cargo calculations prior to discharge
.4 Vessel’s Remaining Onboard (R.O.B.) report upon completion of discharge
.5 Identification of tanks that are crude oil washed during discharge

As will be appreciated, with the foregoing information a fairly clear overview of the conditions prevailing onboard the vessels could be obtained. Together with the foregoing data and by comparison with the diverse analysis results of the cargo’s physical parameters, the manner in which the cargo was behaving during the transportation period could be determined.

3 A brief Review of the Findings so far

3.1 The Volatility of Crude and its Vapour Phase (CRUCOGSA and VOCON Projects)

The vapour phase in a cargo tank system above a crude oil cargo is a very complex mixture of diverse gases which primarily consists of hydrocarbon vapour and Inert Gas. The hydrocarbon vapours are, by definition, a Saturated Vapour mixture whereas, the alternative gases present from the Inert Gas supply are Unsaturated gases. Given these circumstances the differing vapours/gases will behave in different ways with changes in the environment impacting the tank vapour phase e.g. solar warming of the Inert Gas, movement of the vessel causing hydrocarbon vapours to evolve and heating or cooling of the cargo by the surrounding seawater.

Before discussing this issue further, it is important to explain two initial findings that relate to the volatility parameter currently used to inform on the criterion of hydrocarbon vapour pressure; namely, the Reid Vapour Pressure. It was noted that, by undertaking a comparison with historical data for crude oils and the analytical findings for this parameter for the CRUCOGSA load port samples, it would seem that there has been an increase in the volatility of crude oils shipped by sea over the previous 10 to 15 years.

Furthermore it was found that, contrary to the expectations for the behaviour of saturated vapours – they should remain at constant pressure, irrespective of the vapour/liquid ratio or relationship – the Reid Vapour Pressure, which is determined at a Vapour to Liquid ratio of 4:1, does not reflect the true vapour pressures to be experienced in a tanker’s cargo vapour system.
Plotting pressure curves for a constant cargo temperature against liquid to vapour ratios, showed on every occasion, irrespective of crude oil type, an inflection occurring creating a marked increase in pressure at a Vapour to Liquid ratio of 0.2:1 (approximately equivalent to an 80% filled tank) – see Figure 1.

Clearly, the extent of pressure to be developed is dependent upon the concentration and compilation of hydrocarbon vapour present in the vapour phase. Notwithstanding this statement and by reference to early findings from the VOCON project, currently being undertaken, it would seem that when plotting the total hydrocarbon concentration in a vapour phase against a cargo tank filling percent the same inflection occurs at roughly the same point (i.e. at 80% full tank) for a non linear increase concentration of hydrocarbon vapours in the vapour space (see Figure 2).

The hydrocarbon profile as shown in Figure 2 can be compared to a series of pressure plots simulating tank filling, as shown in Figure 3. The percent filling for the unsaturated vapour conditions within the cargo (the vapour volume in the cargo tank system is too large to allow a saturated vapour phase to exist) as shown in Figure 2 corresponds closely to the same simulated conditions shown in Figure 3 for pressure. Likewise the percent filling creating an increase in hydrocarbon vapour concentration corresponds to the a similar percent filling recording an inflection in the graph of pressure and percent filling and the subsequent increase of pressure. The comparisons clearly exist but require further investigation notwithstanding the fact that the examples shown relate to two differing crude oil types.

Between the two vertical lines on the Figure 3 plot, the pressure within the simulated cargo tank loading remains nearly at constant pressure. This is the type of behaviour to be expected from a saturated vapour whose pressure is generally dependent upon the liquid phase temperature. However, the saturated vapour pressure generated by hydrocarbon vapours is one source of pressure contributing to the total pressure within the vapour phase. The other pressure is that developed by the introduced Inert Gas whose variable pressure, which is influenced by the varying temperature of the gas phase, must be added to the hydrocarbon vapour pressure to derive the total gas pressure within the tank system at the time.

Before continuing with this line of discussion, it important to identify certain aspects of tanker operational practice and the constraints of pressure necessitating the release of vapour from a tankers cargo tank vapour system. A tanker’s cargo tank system can only tolerate a certain degree of over pressure (gauge pressure) due to the nature of the design and construction of the cargo tank structure. In order that excessive pressures do not occur within this structure, which could cause damage to the structure, pressure/vacuum valves (P/V valves) are provided for each cargo tank. P/V valves normally have an over pressure relief setting of approximately 1500 mm of Water Gauge (roughly equivalent to 16.7 psia). However, from a general review of information received from participating vessels to the CRUCOGSA research project, a vessel’s command does not rely upon these safety valves and generally controls the pressure within the cargo tanks by manual releases. Normally the selected pressure that would instigate a release of pressure would be between 1000 and 1200 mmWG.

By reference to a selection of voyage data from the overall CRUCOGSA database it is possible to review the behaviour of the vapour space of a volatile crude oil cargo during a voyage of 45 days. The graph reproduced as Figure 4 shows the diurnal pressure fluctuations occurring within the vapour space onboard the vessel and the variations of the cargo temperature which in turn determine the extent of the True Vapour Pressure (TVP) of the hydrocarbon vapours.
Given that a Saturated Vapour pressure is dependent upon the liquid phase temperature then the diurnal fluctuations in pressure, as can be seen from Figure 4, must be due to the unsaturated gas component (the Inert Gases) within the vapour phase of the cargo tank system being heated during the day and behaving in compliance with the Ideal Gas Law/Boyle’s Law.

Figure 4 also records the numerous attempts by the vessel’s command to control the tank vapour pressure with regular manual releases of vapour to atmosphere (see when the tank pressure is reduced to between 500 and 600 mmWG). At the present time a vessel’s command can determine when it is prudent to release vapour due to potential over pressure within the cargo tank system but they have no method or guidelines by which to determine when to stop the release. Clearly by releasing vapour to a pressure below the True Vapour Pressure of the cargo at the time (given a cargo temperature) will only cause more hydrocarbon vapour to evolve from the cargo until equilibrium is restored (the TVP of the cargo is achieved) in the vapour system of the cargo tanks which occurs within a short period of time after the release. To resolve this problem, modelling has been undertaken using the CRUCOGSA analytical database in order to derive an equation that could approximate the True Vapour Pressure to be encountered given both the Reid Vapour Pressure of the cargo and the cargo temperature. The model developed simulates the True Vapour Pressure that would be experienced in a cargo tank system filled to 98%. This model is under refinement by the addition of a third dimension; namely, the percent liquid filling of the cargo tank system.

Alternatively to the foregoing and by examining the manner in which the pressure declines during a controlled/manual release, the True Vapour Pressure of the cargo can quickly be recognised. Figure 5, appended hereto, shows a plot of pressure versus time during a controlled release of pressure through a vessel’s P/V valve.

From figure 5 it can be seen that there are two gradients for pressure decline versus time. The first part of the release shows a more rapid decline in pressure and it is this element or partial pressure of the total pressure that is in excess of the True Vapour Pressure of the cargo (equilibrium pressure) in the vapour system. The subsequent gradual decline shows the liquid phase trying to maintain the equilibrium pressure but the rate of evolution of vapour from the liquid phase is less than the rate of vapour release through the vapour system. Thus, by monitoring the rate of pressure decline with time the vessel’s command can determine when vapour release should be stopped, namely at the equilibrium pressure.

By use of such a procedure and by reference to Figure 5, it can be seen that a large proportion of the currently released vapours could be retained onboard tankers. An integration calculating the excess release area under the pressure plot could suggest a saving of about 80% of released vapours.

This paper has identified above one operational method to reduce the emissions during the transportation of a crude oil but other technical solutions to this general form of environmental pollution are also available. The INTERTANKO VOCON Operational Procedure is based on these observations. (see Annex 2)

During the loading of a crude oil vapours from the previous cargo are present in the cargo tanks. These vapours are those that evolved during the storage and discharge of the previous cargo together with vapours generated as a result of crude oil washing. By reference to Figure 2 and the hydrocarbon concentration at zero percent loading the extent of these vapours can be identified for the specific event. Research is currently under planning to investigate and attempt
to reduce this extent of these vapours to a minimum by investigating the current methods, procedures and equipment involved with Crude Oil Washing that should create more effective methodology and equipment for the completion of this operation (ref: CRUCLEAN project).

During the loading of a cargo further hydrocarbon vapours evolve as a result of the rate of loading and the induced turbulence in the incoming oil. Ultimately the majority of these vapours will be displaced from the cargo tanks by the incoming liquid but the concentration of the VOC will vary in accordance with the True Vapour Pressure of the incoming cargo and the size of the vapour volume in the tank upon completion of loading – see Figure 2 for the varying hydrocarbon concentration during tank filling.

From an operational perspective there is little that can be done to limit the displacement of these vapours. In order to avoid this form of atmospheric pollution it seems necessary that additional equipment and technology must be used to capture these displaced vapour volumes. Currently this is undertaken by the installation and use of a prescribed Vapour Return Pipeline and Connection (Annex VI – Regulation 15). However, the number of loading installations having a Vapour Emission Capture (VEC) systems for crude oil cargoes are limited and for certain cargo operations taking place offshore (FSO, FPSO and Lightering) there is very limited access to a VEC system. Further there are commercial consequences to be associated with the use of shore based VEC systems which relate to the redelivery of a small proportion of the measured delivered volume to a vessel thereby impacting the validity of the declared Bill of Lading quantity.

Pursuant to this various forms of shipboard VEC systems have been designed which predominantly rely on either one of two principles; namely, Absorption/Adsorption of the displaced vapours or the condensing of the displaced vapours for storage onboard in separate deck tanks. Figure 6 shows a schematic layout of a condensing system which relies upon Liquid Nitrogen as the coolant source for condensing the diverse forms of displaced hydrocarbon vapours to liquid for separate storage in gas tanks on deck.

Transportation losses can also be addressed similarly. Equipment has been developed and installed on a tanker that utilises the Adsorption principle for the recovery of the excess vapours. However, by equating the required operational pressure for a tanker’s structure (say 1000 mmWG) to the vapour pressure developed by a crude oil type then the controlled release of vapour will not become a necessity. As can be seen in Figure 1, by increasing the vapour ratio, the True Vapour Pressure decreases quite rapidly until the liquid to vapour ratio of 1:0.2 is reached. Clearly the reduction of cargo input into a tanker would not be a sensible economic solution but such a situation would reduce the equilibrium vapour pressure. An alternative and more satisfactory solution would be to allow the vessel to load a full cargo but to increase the vapour volume so as to reduce the developed vapour pressure. This can be done by adopting a design similar to that shown in Figure 7.

The design concept shows an increased vapour phase but still allowing the vessel to load a full cargo in the “normal” tank volume. The increased vapour volume would represent an addition tank volume, not used for loading liquid, of about 15%. An examination of Figure 7 reveals other features that would assist with the total vapour pressure to be experienced within the vapour space; namely the diurnal variation of the pressure contribution from the unsaturate Inert Gas which will vary when heated during the day by the air temperature. The feature concerned relates to a double deck which should prevent the large variations/fluctuations in vapour temperature by utilising the “Thermos effect” of the double deck.
To conclude, although vapour emissions occur the necessary understanding to enable the development of guidelines has been achieved through both the CRUCOGSA and VOCON researches such that operational methods are available to reduce the impact of the extent of emission. Further, by use of the data available technical solutions have been developed such that alternative methods are also available to reduce the risk of emission to negligible levels.

3.2 The Liquid/Sludge Phase (CRUCOGSA and CRUMECON Projects)

The density of a crude oil should be able to give some indication as to likely behaviour during transportation. After all, crude oil types often have the adjective of either Heavy, Light, Medium etc. which suggests their likely comparative Density. This can be very misleading for the Density is the average Density of all the thousands of compounds within a crude oil. A light crude oil could suggest that it contains more volatile component than a medium or heavy crude oil but this is not always the case. It is possible, for example, to have a crude with a “medium” density but has a “dumbbell” distribution of compounds with a larger proportion of volatile component, limited or reduced middle fraction and then a heavy component content. With the consequences and impact that this parameter has upon transportation criteria, it is therefore that the analysis programme for the CRUCOGSA programme included an analysis for molecular weight distribution as determined by use of Gel Permeation Chromatography together with the parameter of Density.

It should also be stated herein that the record of Density for crude oil cargoes is always reported at an international standard temperature of 15 degrees centigrade. As will be appreciated from the presentation below relating to the pour point characteristics of crude oil cargoes, many crude oils exhibit a pour point temperature well above this standard temperature which in turn requires that the reported Density is obtained by regression from a Density measurement at a higher temperature when the sample is solely within the liquid phase region for the crude oil. Problems with regard to the accuracy of this form of regression will be discussed below in this paper.

Before considering the behaviour of Density over the carriage temperature range and the information that can be deduced there from, it is important to make the correlation between Density and the other generally referred to parameter for tanker operations, namely, Kinematic Viscosity. Taking Dynamic Viscosity as the basis parameter for the flow resistance characteristics then:

\[ \text{Dynamic Viscosity} \propto \frac{1}{\text{Density} \times \text{Kinematic Viscosity}} \]

Thus, Density will vary directly with Kinematic Viscosity.

This circumstance can be seen when Figure 8 is examined for the behaviour of Bonny Light crude oil over a typical carriage temperature range. At roughly 18 degrees centigrade the Kinematic viscosity increases rapidly. The reasons for this change in Kinematic viscosity will be discussed in greater detail below in this paper but is it is due the onset of a two phase mixture in the crude oil liquid phase, i.e. a mixture of liquid and partial solid phases. However at the same temperature as the Kinematic Viscosity inflection the plot of Density also inflects creating a non linear gradient over the carriage temperature range. The correlation between these two parameters is quite predictable from the standard form of equation as quoted above but remains new knowledge for maritime crude oil operations.
Given that Bonny Light crude oil is not a volatile type of crude, the form of the plot of density only reveals one inflection over the temperature range. However, by selecting a more volatile crude oil, Arabian Super Light, and reviewing the plot of Density for a similar temperature range (see Figure 9) a secondary inflection occurs at the initial boiling point temperature for the crude oil – i.e. the evolution of the vapour phase.

Thus, by examining the plot of density over a typical carriage temperature range the phase temperature boundaries for a single phase liquid can be obtained for a crude oil. Further, as stated above, due to the profile of the density plot it is clear that difficulties and inaccuracies will occur when regressing an observed density at an elevated temperature back to the standard temperature (15 degs C) especially when using the current form of modelling equation – an Exponential curve.

Returning to Figure 8 and the correlation between Kinematic Viscosity and Density together with the behaviour of these parameters at lower temperatures; this behaviour supplies information as to the sludging potential of a cooling cargo due to the onset caused by precipitation of a solidifying phase. Earlier research together with confirmation available from the CRUCOGSA data allowed the presentation in 1998 of a “new” parameter for crude oil to regulatory authorities – the Cloud Point temperature of Crude Oil.

The Cloud Point temperature of a crude oil is the determination of the temperature at the phase boundary between the single liquid phase and the commencement of a multiphase consisting of a liquid and sludge phase. In other words, this temperature predicts the commencement of precipitation of sludge material from the crude oil cargo due to cooling of the cargo. Clearly, some, if not all, of this precipitated sludge phase in suspension within the liquid phase could deposit on the floors of a cargo tank increasing cargo loss and presents a subsequent pollution threat if not effectively removed by Crude Oil Washing (COW) operations.

With this “new” parameter and a decision making tool for COWing of cargo tanks, a vessel’s command could:

- firstly predict the potential extent of sludging of the cargo tanks with knowledge of the extent of sludge forming material in the cargo (normally paraffin waxes as their basis) and the temperature at which it would start to occur; and
- prepare the necessary wash material to a required temperature to increase the effectiveness of the COW operation – that is remove the sludge from the cargo tanks.

The previous guidelines used the parameter of the crude oil’s Pour Point temperature for this purpose but, as will be readily recognised, this parameter records the completion of this sludging phase; namely, the approach or onset of a total sludge phase which commences at the Cloud Point temperature.

A total amendment of Section 9 of the mandatory Crude Oil Washing Manual was agreed at IMO with the Cloud Point temperature replacing the Pour Point temperature of the cargo/s as the basis criterion for wash stock preparation for the COWing operation. However it was necessary to supply a series of simple methods for a vessel’s command to calculate this critical temperature. A generalised model to calculate this temperature for the normal/mid range type of
crude oils was developed. The final equation needed to use a commonly reported parameter for the cargo and in this regard the cargo’s Pour Point temperature was selected. Thus, the equation is:

\[ \text{The Cloud Point temperature} \ °C = 20.2 \times 10^{0.00708x - 0.1157714} + 8 \]

Where: \( X \) is the Pour Point temperature in Degrees Centigrade

Alternative techniques are also described within the revised section but the most accurate method for the determination of this parameter is by analysis. By undertaking the measurement of 10 Kinematic Viscosities over a range of temperatures that would include the suspected Cloud Point temperature, a graph can be constructed of Log Kinematic Viscosity versus temperature. Such a plot can be seen in Figure 10.

From Figure 10 certain detail can be gained. For example:

- The Cloud Point temperature is that shown by the red vertical line to the “X” axis and not the Blue vertical line. This misinterpretation of the plot can supply a very much lower Cloud Point than is actual.
- The extent of the angle of inflection supplies an indication as to the likely extent of precipitating waxes.
- It is to be noted that the plot shows more than one inflection and this records the fact that this crude oil contains, as with most crude oils, numerous specie of wax each with their own “solidification” or precipitation temperature.

The analysis of the Pour Point temperature of the many samples received during the CRUCOGSA project revealed another important aspect impacting decision making onboard tankers. The analysis procedure for the necessary Pour Point temperature analysis decided that it was more essential to model the actual circumstances that would impact operations onboard a tanker pertaining to this parameter than by following the prescribed test method for this parameter. The differences between the two procedures were the methods used for the preparation of the sample for analysis. The prescribed method requires preheating of the sample in order to remove what is termed “the thermal history” of the sample but in so doing this procedure causes the volatile solvent fractions to be evaporated from the test sample. What was found by the modified test procedure was that the actual Pour Point temperature for a cargo onboard a vessel would be significantly lower than that potentially reported on the Certificate of Quality for the cargo. However, for Crude Oil cargoes having higher Pour Point temperatures the difference between the methods used had no discernible difference with the result to be achieved. Thus, from a cargo heating and pumping perspective the standard Pour Point Temperature result could be misleading for decision making purposes.

4 The Multiphase Model (see Figure 11)

It was recognised that an important working tool that could be supplied to a vessel’s command would be a generalised model for all crude oils that would predict an envelope of temperatures for the efficient transportation of a crude oil cargo. Clearly, the optimum condition of the cargo should be that it is maintained in its liquid phase only. This condition can rarely, if
ever, occur with respect to a crude oil cargo as a vapour phase (pressure) will always be present. However, by supplying a minimum/maximum range of temperatures which should maintain the crude oil liquid volume in a manageable and operationally effective condition should assist in the general planning required for the efficient transportation and discharge of the cargo.

The minimum temperature for the designed model relates to the avoidance of the precipitation of the sludge phase whereas the maximum temperature relates to avoidance of excessive vapour pressure necessitating a hydrocarbon enriched release to the atmosphere. The required input parameters for the model have been restricted to those that are potentially available and recorded on the Certificate of Quality for the specific cargo/es or are contained in Annex 1 of the Institute of Petroleum publication “Petroleum Measurement Paper No.8 – Guidelines for Crude Oil Washing of Ship’s Tanks and the Heating of Crude Oil being Transported by Sea”.

The Parameters are:

- The Reid Vapour Pressure (p.s.i.a.) – to determine the maximum temperature
- The Pour Point Temperature (°C) – to determine the minimum temperature.

Before discussing the model and its function it is important to clearly identify the model’s limiting functions, i.e. on which occasions and where it can be used. These are primarily:

.1 The temperature guidelines associated with pressure relate ONLY to a 98% cargo loaded condition (further work is being undertaken to further develop this aspect for all loading percentages).

.2 Two variations of Pour Point temperature are available subject to the method used to determine the parameter (reference the discussion above relating to the analytical procedure used for the measurement of the Pour Point temperature).

How to use the Model

On the vertical axis of the model inputs can be made for either type of Pour Point determination (both by the standard method or without the pre-treatment by heating – see above for explanation) or the Reid Vapour Pressure. For the purposes of explaining the use or operation of this model an artificial crude oil has been selected with a Pour Point temperature of -3 °C and a Reid Vapour Pressure of 7 psia.

Taking the Pour Point parameter first, and following the example shown on the model, an input Pour Point of –3 °C is made. Follow the dotted line horizontally across until it intercepts with either of the cloud point curves. The first curve reached represents the Cloud Point or lower temperature for a Pour Point obtained without the pre-treatment process whereas the second curve represents the Cloud Point associated with a Pour Point temperature obtained in compliance with the standard testing method (e.g. I.P. 15). The associated temperatures for both intercept positions are either 17 or 22 °C respectively. These temperatures are the lower temperature for the final temperature envelope for which, if the cargo temperature is above the determined temperature, no sludge deposits should be expected.
Before considering the upper temperature and the associated options available, it is worthwhile pointing out the consequences of the loss of the solvent or volatile components in the crude oil with respect to both its Pour Point temperature and Cloud Point temperature. As can be seen the calculated Cloud Point temperature is lower with solvents present when compared with the situation when some of the solvent is lost during the heating process thereby causing disequilibrium within the crude oil liquid volume phase. If the Cloud Point temperature becomes higher as a result of the circumstance of heating a crude oil liquid then, it follows that the Pour Point will also suffer in the same manner and direction. From an operational perspective this circumstance is well worth noting when considering the behaviour of crude oil for pumping of a heated cargo, its preparation/heating for use as a crude oil washing stock, and its saturation of sludges upon recovery into the slop tanks when used as a wash medium, amongst many other operational circumstances.

The maximum value for the temperature envelope is obtained for the temperature of the liquid. This temperature will determine when the required vapour pressure from the model and could be that it requires a vapour release if the higher pressure requirement is selected. The model supplies two pressure options with regard to this criterion; namely, the temperature that will develop a saturated vapour pressure equivalent to 0 mmWG or 1000 mmWG for a 98% full cargo volume.

Thus, reverting to the example type crude oil with the Reid Vapour Pressure of 7 psia, it can be seen from the model (figure 11) that a maximum liquid temperature of either 32 or 35 °C will supply the respective saturated vapour pressures in a 98% full cargo tank system in order to achieve a tank pressure of either 0 mmWG or 1000 mmWG in the tank vapour system.

With regard to the vapour phase and its associated pressures it is worthwhile stating again that the observed pressures within the cargo tank system will not be limited to those of the saturated vapour pressure generated by the cargo but will also consist of the variable pressures generated by the unsaturated inert gases in the cargo tank vapour system. Therefore, dependent upon the extent of use and presence of inert gas in the cargo tank vapour system, the vapour pressures will vary over a day with the maximum pressures being achieved when the inert gas component is at its warmest. This variation of unsaturated pressure will not immediately impact the underlying saturated vapour pressure generated from the hydrocarbon vapours but will only add to the total recorded vapour pressure in the tank vapour system.

Thus, by attempting to maintain the example crude oil between the temperatures of, say, 22 and 35 °C, a manageable liquid phase will be maintained within the cargo tank system.

5 Conclusions

The CRUCOGSA research project has provided a large data source for the behaviour of Crude Oil whilst being transported by sea. A start has been made in order to examine, interpret and interpolate the diverse data into working models that could assist and guide a Tanker’s command with decision making for the diverse operations that take place on board such a vessel. Much more work is needed to confirm initial findings and develop better tools for those charged with the responsibility of the transportation of this important source material by sea.
Current research is currently being undertaken into both the Vapour behaviour (the VOCON project) and liquid behaviour (CRUMECON project) of crude oils so as to minimise any adverse impacts upon the environment due to its transportation and increase the effectiveness of the transportation process.

The effectiveness of tank cleaning (CRUCLEAN Project) in order to reduce corrosion and the threat of an unwanted pollutant remains high as a planned research project. With the commencement in the 1980’s of Crude Oil Washing of cargo tanks to achieve clean tanks and remove residues, little thought was apparently given to the behaviour of the wash medium in this process to gain the effectiveness required. With the data now available from CRUCOGSA a fresh look at this operation can supply new criteria that would increase the effectiveness of this operation and reduce the unwanted side effects that can occur by way of excessive vapour evolution during the tank cleaning programme.

References:

Figure 1

Total Vapour Pressure Isotherms at different Vapour to Liquid ratios

- Champion
- Forcados
- Palanca
- Brent
- Maya
- Oman
- Iranian Light
- Arabian Super Light
- Arabian Light

Vapor to Liquid Ratio
Pressure (psia)
VOC (%) During Loading of Bonny Light and Brass River Crude Oils

Increased Vapour concentrations creating increased Pressure

Diffusion of Vapour from First Crude Oil whilst awaiting commencement of Second Crude Oil

Unsaturated Vapour Conditions
Figure 3

Isotherms for Iranian Heavy Crude Oil at 20, 30, 37.8 and 45 degrees C
Simulation of Pressure increase during loading
Figure 4

Crude Oil Voyage Data for a Volatile Crude oil
Cargo Temperature versus Tank Pressures

P/V Valve Opening Pressure

Maximum Normal Control Operating Pressure before Manual Release by Vessel's Command
Vapour release of Arab Light crude Oil through a P/V Valve

Equilibrium Pressure

Pressure determined by Vessel for closing the P/V Valve
FLOW CHART for a VEC System for Current Tanker Operations

To Mast Riser, cargo tank inerting or IG dewatering process - Sheet 2

"Top up" Gas Return Line to Cargo Tanks - Sheet 2

Copyright - T.J. Gunner, April 2000 - deemed part of U.K. Patent Application No. 0018374.9
Figure 7

98% Filling Level

Traditional Tank Deck Level

Double Deck offering “Thermos Flask effect” to the vapour space

98% Filling Level
Density Relationship with K. Viscosity for Bonny Light Crude Oil
Sample No. 1032

Figure 8
Figure 9

The Behaviour of Density over the Carriage Temperature Range
Arab Super Light

\[ y = 0.0005x^3 - 0.0211x^2 - 0.4121x + 791.79 \]

Temperature Deg C

Density kg/m³

Water Corr. Density
Poly. (Water Corr. Density)

Initial Boiling Point Temperature inflection – commencement of vapour phase separation

Cloud Point Temperature inflection
Figure 10

Daquing Crude Oil
Log K. Visc diagram
sample nos 349 & 351

The Size of the Angle of Inflection is indicative of the amount of wax in the crude oil
An Optimum Temperature Model for the Transportation of Crude Oil by Sea
ANNEX 2

INTERTANKO VOCON OPERATIONAL PROCEDURE
A Shipboard Procedure for the Control of Atmospheric Pollution
by Volatile Organic Compounds and Reducing Loss of Cargo

Objective

To reduce the extent of emissions of volatile organic compounds (VOC) in the event that a release of gas pressure is required to be undertaken from the cargo tanks on board a crude oil tanker during her loaded voyage.

To limit the extent of cargo loss and the impact of these gases/vapours as an air pollutant.

Background

When transporting crude oils, particularly at the start of a loaded voyage, a large build up of “gas” pressure can be registered on the Inert Gas pressure gauge either on the vessel’s bridge or in cargo control room. This increase in pressure prompts the vessel’s command to instigate a controlled release of “gas” either through the vessel’s Mast Riser or by opening one of the vessel’s P/V Valves. This controlled release is often undertaken when the “gas” pressure within the Inert Gas system approaches the pre-set opening pressure of the vessel’s P/V Valves (these valves are normally set at approximately +/-1500 mmWG).

Thus, a vessel’s command can establish when and at what pressure a manually controlled release of pressure becomes necessary for the safe operation of the vessel. However, a vessel’s command does not know when or at what pressure a manually controlled release should be stopped. Without this information or guidance, excess cargo vapours can be unnecessarily released to the atmosphere causing a loss of cargo and air pollution.

INTERTANKO, Safety, Technical and Environmental Committee (ISTEC) has therefore developed this Operational Procedure that Members of INTERTANKO are invited to consider to implement as a normal routine onboard their vessels that requires no additional equipment other than that currently available onboard a tanker.

This procedure recognises the presence of the two differing types of “gases” (the Unsaturate gas from the Inert Gas supply and the Saturated Hydrocarbon vapours from the crude oil cargo) present in the vapour system and utilises their differing physical behaviour to determine when the manually controlled release should be stopped in order to avoid the unnecessary release of Hydrocarbon vapours to the atmosphere. To understand the background for this procedure and the physical behaviour of the “gases” present, reference to the INTERTANKO publication “Guidelines for the Control of a Multiphase Crude Oil Cargo for Cargo Operations and Handling” is recommended.
By reference to either Figure 1 or 2, this procedure requires the monitoring and the recording of the pressure drop during a release of gas from the cargo tank vapour system. This can be undertaken with the use of the Inert Gas pressure gauge in the cargo control room or, as available, located on the Inert Gas pipeline on deck. Figure 1 records a typical pressure release pressure drop profile using a P/V valve whereas Figure 2 shows a similar profile using the Mast Riser.

![Figure 1: a P/V Valve Release](image1)

![Figure 2: a Mast Riser Release](image2)

**The VOCON Procedure**

.1 Before opening the either the Mast Riser or a P/V valve on deck, note the pressure in the Inert Gas pipeline system.

.2 Open the pressure release valve and record/monitor the pressure within the Inert Gas pipeline at regular short intervals (every 30 seconds for a Mast Riser release or every minute for a P/V Valve release).

**Note**

*Undertaking a pressure release through a P/V valve, by manually opening the pressure system on the valve, will supply a greater degree of control of the pressure drop profile throughout the release period due to the smaller pipeline connection to the designated P/V valve.*
.3 Plot the pressure drop profile and this can be achieved either manually or by use of the Inert Gas Oxygen and Pressure Recorder in the Cargo Control Room but an increase in the Recorder paper feed rate will be required to achieve definition of the plot.

.4 When the rate of pressure drop becomes constant (after the initial rapid pressure drop) then the gas release should be stopped and the valve closed.

.5 Monitor the Tank Gas Pressure after completion of the controlled release in order to check the final pressure obtained within the Vapour/Inert Gas system.

Advice Notes

a) *A review of figures 1 and 2 show a clear change in the rate of pressure drop during the release period. If the gas release continues after this point then the pressure in the Inert Gas system will be quickly restored to the pressure associated with the point where the rate of pressure drop changes (the Red horizontal line on Figures 1 and 2).*

b) *If there is a Straight line drop of pressure observed and no inflection observed by 800 mm WG, then close the release valve anyway.*

c) By reference to the ISGOTT Publication, all safety measures should be taken to minimise the hazards associated with vented gases from the vessel’s cargo tank system.