Health quality assurance approaches for bitumen manufacture and supply

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ABSTRACT

In 2011, IARC conducted its review of bitumens. IARC published its review in mid-2014 and highlighted its concern that occupational exposure to bitumen and its emissions includes low levels of polycyclic aromatic hydrocarbons (PAHs). IARC's rationale included mechanisms of carcinogenesis involving PAHs. While major reductions in occupational exposure to bitumen/emissions was recognized by IARC, further effort in this area was encouraged. Within this context, manufacturers and suppliers of bitumen can take steps to assure that the content of PAHs in bitumen are minimized. A few conceptual examples follow.

Bitumen is often assigned CAS# 8052-4-42/EINECS 232-490-4. The description for this substance indicates that the hydrocarbons are "predominantly greater than C25". Eurobitume, in its Guidance on Manufacturing Process for Use in REACH Registrations (2008), provides an interpretation that recombination of streams consistent with this definition can be considered the substance asphalt. In practice, "predominantly" could be interpreted in different ways. A consistent interpretation that "predominantly" meets a specific target, e.g., >80%, can be useful in excluding undesirable lower boiling hydrocarbons, including some PAHs. As further noted in the Eurobitume Guidance, blending of streams that do not meet this definition could result in a mixture. Under classification criteria, if such a stream is a Category 1 carcinogen, e.g., a PAH-rich stream, and at >0.1%, then the mixture would be considered carcinogenic. While this is broadly understood for product manufacture, it may also have utility in decision making regarding potential contamination scenarios that could occur either in a plant or transportation. Lastly, standards can also be established to assure the safety of blend streams. For example, residual aromatic extract (RAE) substance EC 265-110-5 (CASRN 64742-10-5), is a potential blend stream for bitumen. CONCAWE established that RAE classification as a carcinogen needs not apply if it can be shown that the substance has a mutagenicity index (MI) less than 0.4 as measured by ASTM E 1687-04 or if another predictive test demonstrates that the substance is not carcinogenic. We demonstrated a relationship (patent pending) between MI and distillation, such that a distillation measurement (5%GCD) can be used as a predictive test and quality assurance tool.

Keywords: Health Safety and Environment, Polycyclic Aromatic Hydrocarbon, Risk management

Health Quality Assurance Approaches for Bitumen Manufacture and Supply

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In 2011, IARC conducted its review of bitumens. IARC published its review in mid-2014 and highlighted its concern that occupational exposure to bitumen and its emissions includes low levels of polycyclic aromatic hydrocarbons (PAHs). IARC included a rationale based on mechanisms of carcinogenesis involving PAHs. While major reductions in occupational exposure to bitumen/emissions have been achieved, and were noted by IARC, further effort in this area was encouraged. Within this context, manufacturers and suppliers of bitumen can take steps to assure that the content of PAHs in bitumen are minimized. A few conceptual examples follow.

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Keywords: Health Safety & Environment, Polycyclic Aromatic Hydrocarbons, Risk Management

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) can be found in relatively low concentrations in bitumens and its emissions. Some PAHs are carcinogenic, and are believed to have a central role in cancer potential reported to be related to occupation exposures to bitumens and bitumen emissions (International Agency for Research on Cancer (IARC), 2011). It follows that practices that reduce or minimize potential exposure to the PAHs would also reduce potential risk. IARC noted a strong trend of exposure reduction and recommended that this be continued. This paper discusses some possible approaches to bitumen product management with the purpose of minimizing potential exposure to PAHs.

2. EUROBITUME GUIDANCE

Eurobitume (2008) published its "Guidance on Manufacturing Process for Use in REACH Registrations". This document provides a basis for defining, and distinguishing between, bituminous substances and preparations (mixtures) under REACH. As an example, bitumen substances are often assigned CAS# 8052-42-4/EINECS 232-490-4. The definition for this substance is

> A very complex combination of high molecular weight organic compounds containing a relatively high proportion of hydrocarbons having carbon numbers predominantly greater than C25 with high carbon to hydrogen ratios. It also contains small amount of various metals such as nickel, iron or vanadium. It is obtained as the non-volatile residue from distillation of crude oil or by separation as the raffinate from a residual oil in a deasphalting or decarbonisation process.

The Eurobitume Guidance outlines how a substance meeting this definition can be produced by alternative means of distillation, separation, and recombination of heavy streams meeting the definition of asphalt 8052-42-4. A key feature of the definition is that the hydrocarbons are "predominantly greater than C25". This criteria thus excludes smaller (lower molecular size, weight and distilling) molecules including some potentially toxic PAHs. But the word "predominantly" is imprecise and subject to interpretation. Selection of a specific interpretation of "predominantly" may be useful in providing a consistent target for manufacturing as well as other potential uses. To the extent that a consistent target excludes potentially toxic molecules is a health benefit.

To illustrate further, and using a so-called "80/20" rule, the word "predominantly" could be interpreted as being 80%. That is, an asphalt stream would then contain >80% hydrocarbons greater than C25. Such a se guideline facilitates best practices to assure that side streams used in manufacturing as well as the finished bitumen are all consistent with the Eurobitume guidance. It can be further noted that a >80% guideline is more stringent at excluding smaller hydrocarbons than if predominantly were interpreted as lower limits such as >60%, or >51%, and a >80% target would better exclude smaller hydrocarbons. Also, as it is generally recognized that PAH-distribution is bitumen is largely in the distillation front-ends, a relatively stringent definition of predominantly should better exclude such molecules than a less stringent, or inconsistent practice.

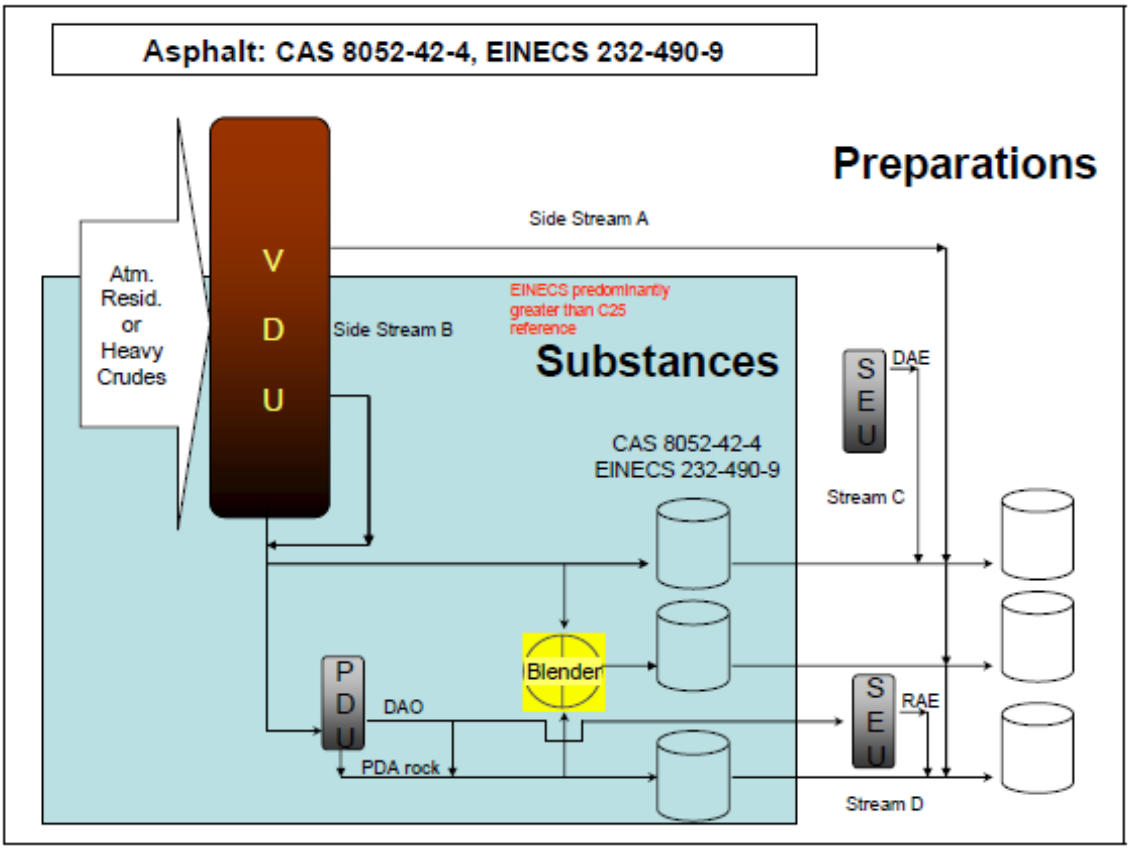

Figure 1: Asphalt Substances Manufacture. Eurobitume, 2008.

3. GLOBAL HARMONIZED SYSTEM (GHS) FOR CLASSIFICATION OF CHEMICALS

Typical classification criteria require the identification of hazardous substances, such as carcinogens, in mixtures. Petroleum streams are UVCB substances (IPIECA, 2010), that is, "unknown or variable composition, complex reaction products and biological substances". UVCB substances including petroleum streams are described and classified consistent with their CAS# and EINECS# descriptions. Thus, consistent with prevailing classification schema, any bitumen prepared as a mixture containing more than one substance including a classified hazardous substance would need to also be classified as hazardous if defined classification thresholds are exceeded. For carcinogenic substances, including UVCBs, the typical thresholds are 0.1 or 1.0%, depending upon the specific carcinogen classification. While this is broadly understood in manufacturing of bitumens, it may be less understood in occurrences of unintentional mixtures, for example in cases of contamination. As an example, bitumens are often transported via barge or tanker, often owned by a third party company. These vessels may not be dedicated to shipment of bitumens, and may have contained previous cargoes, possibly hazardous cargo. Transport of product is not excluded from classification criteria. Thus, a prior cargo of a classified ("toxic") substance would impart those same characteristics onto the bitumen placed into the vessel if residual amounts exceed the classification criteria. Practical knowledge of this, and application of both the regulatory classification schemes as well as the Eurobitume guidance as to how bitumen is defined, can provide confidence that the product in transport does not require classification. For example, decisions could be made to dedicate shipping vessels or arrange for cleaning. Best practices can be conceived to manage potential contamination scenario in a way that classification requirements and assurance of health protection are achieved.

4. RESIDUAL AROMATIC EXTRACTS

Residual Aromatic Extract (RAE, CASRN 64742-10-5, EC 265-110-5) is a potential blend stream for bitumen. It also can be used as a flux during air-blowing for the manufacture of oxidized asphalt. RAE is an aromatic oil derived from vacuum residuum. As such, it may contain PAHs, although due to distillation considerations, at much lower concentrations than for aromatic oils derived from distillate streams (Distillate aromatic extracts, (DAE), CONCAWE (2014).

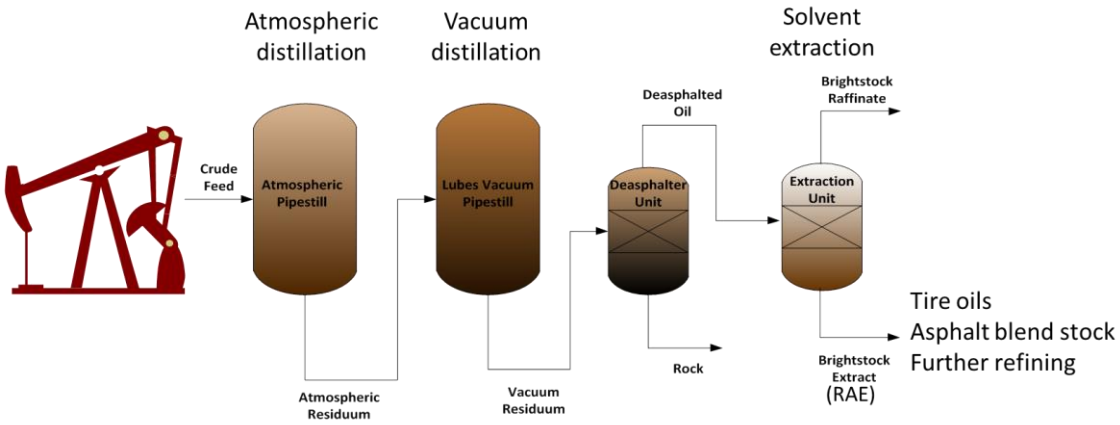

Figure 2: Simplified RAE Refining Process.

CONCAWE (2014) established that RAE classification as a carcinogen need not apply if it can be shown that the substance has a mutagenicity index (MI) less than 0.4 as measured by the test method described in ASTM E 1687-04 or if another predictive test demonstrates that the substance is not carcinogenic. In practice, obtaining an MI determination may not be timely for asphalt production, because it requires a specialized laboratory as well as several days to weeks to complete and report analysis. An alternative approach was developed by ExxonMobil in which we demonstrate that the MI of a RAE can very carefully be controlled to the required range by limiting the distillation profile of the stream (Sircar et al., 2015; Kung et al., 2014). The authors collected both MI and 5% distillation temperature by gas chromatography distillation (GCD) for residual derived materials, i.e., deasphalted oil, residual aromatic extract, and raffinate. Figure 3 shows a strong correlation between MI and the 5% gas chromatographic distillation, with an $r^2 = 0.757$.

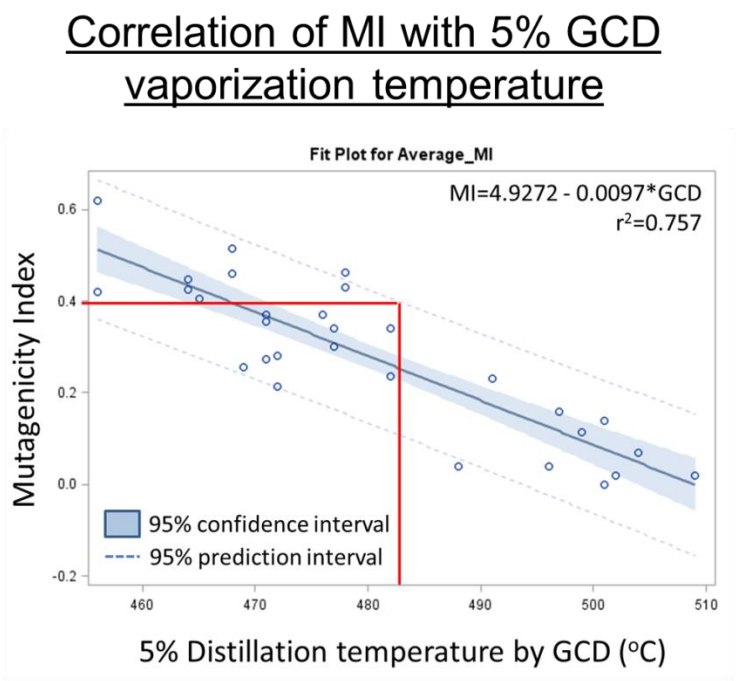

Figure 3: Correlation of MI with GCD. Linear regression of the MI/GCD (5%) is shown. As the temperature threshold is increased, the average MI decreases.

These data permitted identification of the 5%GCD that would correspond to an MI = 0.4, that is, to a criteria for non-carcinogenicity. Using the upper bound of the dose response curve, as is common practice in health risk assessments, it is identified that an RAE with a 5%GCD > 482°C would be identified as having an MI < 0.4 and therefore, likely non-carcinogenic. A second statistical analysis of the data was conducted to assess the probability that any given 5%GCD would correspond to an MI < 0.4. This result is shown in Figure 4, and consistent with the analysis shown in Figure 3, it was determined that a 5%GCD of 482oC has a Probability of 95% of an MI < 0.4. Thus, use of 5% GCD of the RAE provides a rapid, "real-time", means to quality assure the stream. That is, rather than submitting samples for mutagenicity testing and likely waiting weeks for results of pass/fail, the 5% GCD can be determined very rapidly and facilitate release of product in a more timely manner.

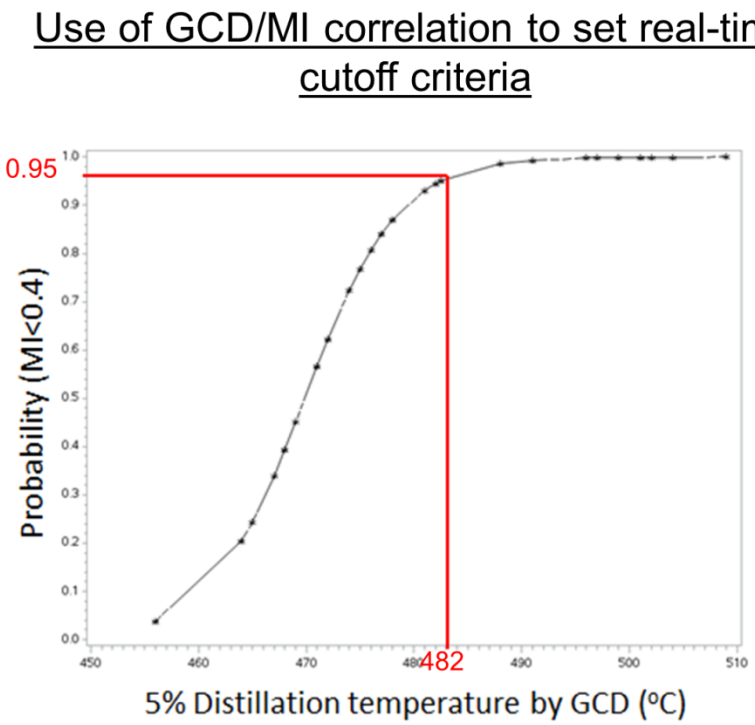

Figure 4: Increasing Probability of a Non-mutagenic Result with Increasing GCD 5% cutoff. As the GCD 5% cutoff threshold is increased, the probability of samples' MI being < 0.4 increases. At 482°C, the probability MI<0.4 is 95%.

5. SUMMARY AND CONCLUSIONS

Bitumens can be manufactured, blended and transported in a number of ways. Along this entire cycle, there are variables that, if unmanaged, can potentially result in health hazard potential greater than that of a typical straight run bitumen. Technical and management approaches can be derived to control these variables and facilitate the common goal of reducing and managing occupational exposures. Three promising approaches to managing product quality include i) consistently interpreting the extent to which the asphalt (CASRN 8052-42-4) contains predominantly greater than C25 hydrocarbons and hence, minimizes "light ends", ii) assuring that cargoes and potential contamination cases meet the same hazard classification criteria used for refinery streams, and iii) application of specific quality control parameters to potential blend streams.

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