Research report

A review of methods for estimating annual VOC emissions from refinery effluent water systems

RESEARCH REPORT

A REVIEW OF METHODS FOR ESTIMATING ANNUAL VOC EMISSIONS FROM REFINERY EFFLUENT WATER SYSTEMS

1st edition

March 2011

Published by
ENERGY INSTITUTE, LONDON
The Energy Institute is a professional membership body incorporated by Royal Charter 2003
Registered charity number 1097899

The Energy Institute (EI) is the leading chartered professional membership body supporting individuals and organisations across the energy industry. With a combined membership of over 14 000 individuals and 300 companies in 100 countries, it provides an independent focal point for the energy community and a powerful voice to engage business and industry, government, academia and the public internationally.

As a Royal Charter organisation, the EI offers professional recognition and sustains personal career development through the accreditation and delivery of training courses, conferences and publications and networking opportunities. It also runs a highly valued technical work programme, comprising original independent research and investigations, and the provision of EI technical publications to provide the international industry with information and guidance on key current and future issues.

The EI promotes the safe, environmentally responsible and efficient supply and use of energy in all its forms and applications. In fulfilling this purpose the EI addresses the depth and breadth of energy and the energy system, from upstream and downstream hydrocarbons and other primary fuels and renewables, to power generation, transmission and distribution to sustainable development, demand side management and energy efficiency. Offering learning and networking opportunities to support career development, the EI provides a home to all those working in energy, and a scientific and technical reservoir of knowledge for industry.

This publication has been produced as a result of work carried out within the Technical Team of the EI, funded by the EI's Technical Partners. The EI's Technical Work Programme provides industry with cost-effective, value-adding knowledge on key current and future issues affecting those operating in the energy sector, both in the UK and internationally.

For further information, please visit **http://www.energyinst.org**

The EI gratefully acknowledges the financial contributions towards the scientific and technical programme from the following companies

BG Group
BP Exploration Operating Co Ltd
BP Oil UK Ltd
Centrica
Chevron
ConocoPhillips Ltd
EDF Energy
ENI
E. ON UK
ExxonMobil International Ltd
Kuwait Petroleum International Ltd
Maersk Oil North Sea UK Limited
Murco Petroleum Ltd
Nexen
Saudi Aramco
Shell UK Oil Products Limited
Shell U.K. Exploration and Production Ltd
Statoil Hydro
Talisman Energy (UK) Ltd
Total E&P UK plc
Total UK Limited

However, it should be noted that the above organisations have not all been directly involved in the development of this publication, nor do they necessarily endorse its content.

ISBN 978 0 85293 602 3

Published by the Energy Institute

Further copies can be obtained from: Portland Customer Services, Commerce Way, Whitehall Industrial Estate, Colchester CO2 8HP, UK.
t: +44 (0)1206 796 351 e: **sales@portland-services.com**

Electronic access to EI and IP publications is available via our website, **www.energyinstpubs.org.uk**.
Documents can be purchased online as downloadable pdfs or on an annual subscription for single users and companies.
For more information, contact the EI Publications Team.
e: **pubs@energyinst.org**

CONTENTS

FOREWORD

This Report reviews the methodologies available in the public domain to estimate emissions from refinery effluent water systems. This review was undertaken as part of the updating of the Energy Institute (EI) *Protocol for the estimation of VOC emissions from petroleum refineries and gasoline marketing operations*. The second edition of this Protocol was published in 2010.

There were particular concerns that the emission factor for gravity type (API) oil-water spearators in the first edition of the Protocol was no longer representative of current operating conditions and could potentially be conservatively high.

Because the intent of the Protocol is to provide simple emission estimation methodologies for annual inventory compilation purposes, the reasonableness of the existing emission factors in the first edition of the Protocol are considered in detail. The main components of the water treatment system are reviewed, but with emphasis on API type oil-water separators as these are the norm in UK refineries. Measurement of emissions from effluent water systems is difficult, expensive and has the potential for significant errors when converting concentration measurements to fluxes. These are compounded when extrapolating short term estimates to an annual average as there are considerable temporal variations in flow and oil content in refinery effluent water.

The use of computer models can generate accurate emission estimates representing conditions at the time of data collection. However, the methodologies are data intensive, requiring not only site-specific data but information regarding the physical and chemical characteristics of each of the VOCs emitted. To obtain the requisite site data requires extensive sampling and analyses to be carried out. The poor mixing of some streams and the presence of a free oil layer poses challenges to obtaining the representative samples required to ensure accurate emission estimation.

For the EI *Protocol for the estimation of VOC emissions from petroleum refineries and gasoline marketing operations*, the use of emission factors is adequate for effluent water systems. This Report provides the recommended emission factors that were incorporated in the second edition of the Protocol.

ACKNOWLEDGEMENTS

The following members of the EI's Emissions Working Group have been associated with the production of this Report:

Steve Cross	Shell
Beate Hildenbrand	Energy Institute
Kevin Lenthall	Total
Graham Neal	ExxonMobil
Paul Shawcross	ConocoPhillips
Brian Smithers	Consultant

The EI wishes to express its gratitude to Brian Smithers as principal author, and record its appreciation of the valuable contributions of the Emissions Working Group members.

1 INTRODUCTION

Volatile organic compounds (VOCs) are of concern because of the potential formation of ground-level ozone. This is formed by those compounds that react photochemically with nitrogen oxide.

This has resulted in the promulgation of pan-European legislation which requires reductions in VOC emissions from a range of sources, including a number in the downstream oil industry. To permit the effectiveness of these abatement programmes to be assessed, all industries are required to assist in the compilation of national and international emission inventories, e.g. the European Pollutant Release and Transfer Register (E-PRTR).

The majority of VOC emissions within the oil industry have to be estimated. This is because they cannot be directly measured, being from large diffuse sources e.g. storage tanks, and from point fugitive sources such as equipment components on process plant.

VOC emission estimates are currently made in the UK downstream oil industry using the methodologies provided in the EI *Protocol for the estimation of VOC emissions from petroleum refineries and gasoline marketing operations* [1].

The methodologies presented in the Protocol are intended to provide reasonable estimates of annual emissions without resorting to overly lengthy and/or complicated calculation methods. Thus, in the majority of cases, the Protocol provides a simple calculation or emission factor approach to emission estimation. Only methodologies and factors published in the public domain are included. As the reported average value of VOC emissions for eight UK oil refineries in 2004 was 3,7 kte/year, the Protocol considers sources emitting <10 te/year to be deminimus. The current Protocol, published in 2010 is an update of the first edition (produced in 2000) and contains new and updated emission factors.

The factor provided in the first edition of the Protocol for uncovered gravity separators (e.g. API type) was from a reference dated 1985. Since that time the amount of oil entering refinery effluent water systems has been reduced. This is due, for example, to improved operations during sampling and to the installation of devices to reduce oil loss from containment such as automatic drain valves. In addition, typical values of water temperature, which has a significant effect on the rate of VOC evaporation, are lower in European refineries than those reported by US EPA [2].

These differences would suggest that average emissions from water treatment at UK refineries are now less, per unit volume of water processed, than factors derived in the USA some years ago would imply. Moreover, at the same time the volume of water treated has decreased due to improved effluent water management including, for example, segregation of clean water streams, changes in cooling water systems, reuse of water streams, etc.

There were concerns, therefore, that the emission factor in the first edition of the Protocol for API separators was no longer representative of current operating conditions and could potentially be conservatively high.

Consequently, a review was undertaken of the methodologies available in the public domain for the estimation of emissions from components of the effluent water collection and treatment system. This Report provides the details of that review. Because the intent of the Protocol is to provide simple emission estimation methodologies, these form the focus of this Report. The main components of the water treatment system are considered, but with emphasis on uncovered gravity type (API) separators. These are the norm in UK refineries for the primary treatment of effluent water and are the major emission source in the system.