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### FOULING IN CRUDE OIL PREHEAT TRAINS: A SYSTEMATIC SOLUTION TO AN OLD PROBLEM

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### ABSTRACT

About 6% of the energy content of each crude barrel processed in an oil refinery is used in the refinery itself, of which a large amount is in the crude distillation unit. Heat integration and conservation are therefore paramount. It is well established that one of the major causes of refinery energy inefficiency is crude oil fouling in pre-heat trains. This has been a most challenging problem for several decades, due to difficulties in understanding the fundamental deposition mechanisms and its causes and little knowledge the deposit composition. of Current methodologies for design of heat exchangers tend to just allow for fouling rather than fundamentally prevent it.

To address this long standing problem in a systematic way, the UK Engineering and Physical Sciences Research Council (EPSRC) is funding a large scale interdisciplinary research project, CROF (for CRude Oil Fouling). The project brings together leading experts from of the University of Bath, University of Cambridge and Imperial College London and industrial partners represented via the company IHS ESDU. The project aims at providing a platform to investigate fundamental parameters leading to deposition, to provide a framework for predicting deposition and avoiding it by design and to formulate methods for mitigation. The research effort, involving both experimental and modelling work, is coordinated in 8 sub-projects which examine the fouling problem across all scales, from the molecular to the process unit to the overall heat exchanger network. To make the outcomes of the project relevant and transferable to industry, the research team is working closely with experts from many world leading oil companies.

The systematic approach of the CROF project is presented. Individual sub-projects are outlined, together with how they work together. Initial results are presented, indicating that a quantum progress can be achieved from such a fundamental, integrated approach. Some preliminary indications in respect of impact on industrial practice are discussed.

### **INTRODUCTION**

About 6% of the energy content of each crude barrel processed in an oil refinery is used in the refinery itself. With a global production of about 82-85 million barrels/day, this is roughly equivalent to the entire production of Exxon or Shell to operate the world's 720 refineries. Crude oil distillation, where the incoming crude is first heated up and split into its main fractions, accounts for a large fraction of this energy. Thus, strenuous attempts are made to recover as much as possible of the energy from the product streams of the crude distillation column (and other refinery units) by means of a network of heat exchangers, often called the "pre-heat train" (PHT). A typical crude pre-heat train is illustrated in Fig. 1. Unfortunately, crude oil contains a variety of substances, which tend to deposit as fouling layers in the heat exchangers when heated. The material deposited ranges from gel-like to solid-like and may change its properties with time. The fouling deposit growth results over time in decreased energy recovery and thus increased energy demand (via the furnace prior to the column in Fig. 1), with extra cost of fuel and CO<sub>2</sub> emissions. Occlusion of tubes in the exchangers due to fouling requires extra pumping power to overcome the pressure drops. When the furnace hits its maximum capacity (firing limit) the crude oil throughput must be throttled back, with serious economic impact.



Fig. 1 Schematic diagram of typical crude distillation unit (after Panchal and Huang Fu, 2000).

Periodically, individual exchangers must then be taken out of service and cleaned, again with high impact on production and considerable health and safety issues. Fouling by asphaltenes, waxes and hydrates also has serious implications in areas other than refining. For example, it has caused blockages of several pipelines under the North Sea. The economic cost of crude oil fouling in refinery preheat trains is huge. In the US alone it was estimated at around US\$1.2 billion per annum (circa 1992) (ESDU, 2000), at a time when extra CO<sub>2</sub> emissions were not costed. The cost of pre-heat train fouling in one 160,000 bbl/day Total refinery was estimated in 2003 to be US\$1.5 million in a 3 month period Bories and Patureaux, (2003). One 200,000 bbl/day UK refinery reported recently (April 2009) to the authors that 1°C of loss of preheat (that is, in the oil temperature at the furnace inlet) cost the operator some £250,000 p.a. Other estimates state that the energy equivalent of some 0.25% of all oil production is lost to fouling in the pre-heat train. This translates to close to 1 day's production lost per annum (85 million barrels on a worldwide basis). The principal benefit to the refiners of reducing fouling is increased capacity. Increasing effective on-stream time due to reduced fouling/cleaning can lead to massive savings in some refineries. Polley (personal communication, 2009) reported that the profit loss through reduced production (last quarter of 2008) ranged from around US\$2/bbl in some Texas refineries to up to US\$10/bbl in a refinery processing heavy 'opportunity' crudes and that one day lost production on a 200,000 bbl/day refinery is worth between US\$0.4M and US\$2M. Some older analysis (Van Nostrand et al., 1981) for a then typical 100,000 bbl/day refinery attributes almost 40% of the costs of fouling to reduced throughput. The above estimates must be taken with some care, as they span a period of oil prices ranging from US\$10-150/bbl. Fouling related losses are however important at all oil prices, as they affect directly refining margins and revenue losses.

The impact of crude oil fouling is increasing for all oil companies. Crudes are generally becoming heavier and more complex, yet refineries were generally designed to process the lighter crudes that are today becoming scarcer. The worldwide shortage of middle distillates is also a driver to the processing of heavier, dirtier crudes that have a higher yield of these valuable components. Fouling problems are therefore increasing in severity.

The importance of the crude oil fouling problem evidenced in the above figures led to a number of industrial and academic studies over several decades, focusing on mechanisms and parameters that govern rates of fouling, namely temperature, pressure, oil composition, salinity and fluid velocity. A number of excellent reviews are available (see for example, Taborek *et al.*, 1972, Watkinson, 1988, Watkinson and Wilson, 1997, Taborek 1995, Bott, 1995, Muller-Steinhagen, 1995, Muller-Steinhagen *et al.*, 2005). This research is summarised in Fig. 2 (after Epstein, 1983). Work has been done in a number of major centres. In the USA groups include those at Heat Transfer Research Inc. (HTRI) (Bennet *et al.*, 2006), where a pilot scale facility has been constructed, and at the Argonne National Laboratory



Fig. 2  $5 \times 5$  fouling matrix (after Epstein, 1983). Dark shading indicates areas of high research levels: pale areas where little research has been done.

(ANL) (see for example Ebert and Panchal, 1995; Panchal et al., 1999). Weihe (1999a, 1999b, 1999c) has devised methods of identifying the fouling propensity for selfincompatible and mixed crudes. In Canada, work is proceeding at the University of British Columbia (e.g. Watkinson, 2003; Srinavasan and Watkinson, 2003). In the UK, ESDU (now IHS ESDU) have set up an international Oil Industry Fouling Working Party of oil companies and their suppliers; a major guidance document on crude oil fouling (ESDU, 2000) has been produced under the aegis of this Working Party. Work at Bath (Crittenden et al., 1987, 1992; Takemoto et al., 1999) originally focused on modelling and on the use of model fluids as substitutes for crude oil. More recently, a major test facility was built and a first programme of work completed. Experiments have determined the effects not only of major processing parameters (surface temperature, velocity and heat flux) but also the effectiveness of in-tube inserts (Phillips, 1999). At Cambridge, the focus has been on developing physical measurement methods (Tuladhar et al., 2002; Gu et al., 2009a) and on modelling the influence of fouling in heat exchangers and heat exchanger networks (Yeap et al., 2004). The (then) European Community R&D strategy for, and projects on heat exchanger fouling in general are briefly reviewed in Pilavachi and Isdale (1993).

Although good progress has been made in experimental studies of crude oil fouling, it appears that an asymptotic state of knowledge has been reached. Data-led mitigation is an active area, but this provides a response rather than a cure. Whilst the results are useful, the mechanisms by which the fouling proceeds are still not fully understood. For example, it is generally assumed that materials depositing on heat transfer surfaces are asphaltene derived. These are typically complex mixtures of polynuclear aromatic ring structures, with high heteroatom content; they carry most of the trace element content of the oil. However, it is apparent that only small fractions of the asphaltene content in crudes actually deposit on heat exchange surfaces and that this process can be initiated by other species. There are complex, ill understood interactions between oil properties, phase stability, rheology, chemical reactions, heat transfer, interfacial and adhesion properties, surface properties and exchanger geometry, all of which affect all the mechanisms and sub-processes in the fouling matrix of Fig. 2. What is clearly needed is a much more fundamental approach to the problem. Recognising it is unlikely that this will emerge from the type of studies carried out by and for industry, a fundamental and integrated project was initiated that would address the basic issues but also provide a route for exploiting the findings in industry.

### THE CROF PROJECT

To meet the challenges outlined above, a 3-year CRude Oil Fouling (CROF) project was initiated in June 2006 with substantial funding from the UK Engineering and Physical Sciences Research Council (EPSRC) and industry. The project brought together a multidisciplinary team of experimentalists (carrying out both small- and large-scale experiments), theoreticians (developing new analysis, theory and software in each of the underlying activities), systems engineers (carrying out modelling, component integration and scaling up, and analysis, design, and optimisation studies at plant-scale) and industrial researchers (providing data, materials, advice, assessment, case studies and feedback).

The CROF team comprises academic researchers at Imperial College London, the University of Bath and the University of Cambridge (15 academic staff supervising 10 PhD students and 8 postdoctoral research associates directly funded on this project, augmented by short-term undergraduate and postgraduate projects). From inception, the CROF project also involved a large consortium of multinational companies from the oil-and-gas sector, participating through the Oil Industry Fouling Working Party operated by IHS ESDU, an industrial consultancy based in London. Oil companies in the Fouling Working Party include BP, Chevron, ConocoPhillips, ExxonMobil, Petrobras, PETRONAS, Shell and Total and represent about 70% of the world's refining capacity. Also represented are heat transfer equipment manufacturers (e.g. Alfa Laval, Calgavin) and chemical additive suppliers (e.g. Nalco). Each of the companies is represented by their top internal heat exchange and fouling experts (typically from a central specialised R&D function supporting the worldwide operations of the respective organisations). IHS ESDU coordinates the development of close links with the oil refining industry and their suppliers and ensures the industrial relevance of the proposed work.

The work programme represents a new approach, as needed to advance the subject. The overall problem is tackled via a closely linked set of sub-projects, bringing together a wide range of skills and techniques to produce a co-ordinated attack on this important problem (Fig. 3). Understanding the fouling process requires investigating the temperature dependence of the link between feedstocks and deposits, the advanced characterisation of these materials and examining the relationship between fouling rates and asphaltene (and other species) contents (Sub-Project A).

A fundamental understanding of mechanisms by which deposits adhere to surfaces are developed in Sub-Projects B and the transfer processes which take them there in Sub-Project C. Crucial to all of this is the investigation of the underlying thermodynamic interrelationships.



Fig. 3 CROF sub-projects and some key inter-relations.

Significant advances have been made in understanding the thermodynamics of complex compounds at the molecular level and there is scope for improving the understanding of asphaltene behaviour using these advances (Sub-Project D). Experimental studies of fouling are carried out in two facilities to establish rates of deposition and provide deposit samples for physical and chemical characterisation. The first is a stirred vessel test-facility developed at Bath University (Sub-Project E). The second involves continuous flow tests in an electrically heated annulus test facility at Imperial College, with novel sensing equipment developed at Cambridge (Sub-Project F). These experiments are highly complementary. The use of a stirred vessel allows repeated low inventory tests to be done quickly and economically, enabling the systematic study of a variety of crude oils, flow modifiers and surface conditions. It is also easy to extract samples for analysis under Sub-Project A. The flow tests represent a realistic representation of the situation in a heat exchanger and allow investigating, amongst other phenomena, the effect of fouling deposits on pressure gradients. The flow tests are designed to make continuous measurements of fouling layer thickness and heat transfer coefficients (and thus *fouling* factor) and to study the dynamics of the fouling process. Understanding the physics, chemistry, thermodynamics and associated transfer processes would be of little avail if it did not lead to means of control and mitigation of the fouling problem. Sub-Project G is a joint Cambridge/Imperial College effort on control and mitigation involving advanced modelling of heat exchangers (individually and in network systems) at industrial scale and of cleaning and control strategies. Finally, there is little point in making any advances on this important subject if the technology cannot be transferred efficiently to industry. The bridge to industry is provided by the central role of IHS ESDU in the programme. As noted, they are charged with the task of interfacing with the oil refining companies and their suppliers and transferring the technology by various means (Sub-Project H).

An important feature of the overall programme is its *multi-scale* nature, with inputs ranging from molecular scale to plant scale. By adopting such an approach, new insights and methodologies can be developed through understanding the mechanisms that link the different scales. It was recognised that close integration of the activities is essential in order to reap the maximum benefits, and the structure and

management of the project and team were designed accordingly.

### PROGRESS AND ACHIEVEMENTS TO DATE

To date, substantial experimental results have been obtained in Sub-Projects A and B. Molecular- and continuum-scale modelling developments in Sub-Projects C and D, respectively are continuing apace. The two pilot plant rigs (Sub-Projects E and F) have been designed and built. Some interesting data have already been collected from the batch rig, while the continuous rig is presently being commissioned and tested, with data to follow by the end of the year. Good progress has been made in the development of plant scale models of heat exchangers under fouling and exchanger network applications. The interactions within the team and with industry were developed in a number of ways and are growing well. For presentational purposes, progress and achievements in this section are described according to the sub-projects detailed in Fig. 3. This also reflects the "bottom-up" nature of the implementation work. However, suitable emphasis is made on the strong links between sub-projects and the highly beneficial interplay between them.

## Sub-Project A: Characterisation of asphaltenes and deposited foulants

The main focus of research in this sub-project is to explore whether and how molecular masses and structures of the deposits actually relate to components of the crude oil feed materials and to identify the chemical transformation leading to deposit formation. It focuses on the study of changes in the crude oil leading to fouling, as well as in the chemical characterisation of deposits, both laboratorygenerated and of industrial origin, and liquid phase after the crude oil has been heated. Many techniques have been used to investigate the molecular masses and chemical structures of asphaltenes and other species but no single technique is able to unravel the molecular masses and structures of complex hydrocarbon liquids as each technique allows only a limited, specific view of these complicated materials. For this reason an array of multiple approaches is used.

A batch micro-bomb reactor (MBR) was used to study the effect of time-temperature history of crude oil samples on the formation and deposition of a solid phase (Venditti et al. 2009a). This approach allows firstly, to decouple the transformations induced by exposition of the samples to temperature from flow-related effects, and secondly it enables measuring the effect of different variables on the chemical characteristics of the liquid and the deposits under carefully controlled operating conditions, not available from refinery operation data. Formation of deposits has been studied at temperatures between 280 °C and 390 °C and residence times up to 24 hours. Both the liquid and the solid phase have been analysed by a number of techniques, which include size exclusion chromatography (SEC) (Berrueco et 2008), UV-fluorescence spectroscopy, elemental al. analysis, solubility tests in various solvents and thermo gravimetric analysis (TGA). A process of chemical transformations due to heating was observed to take place in both the fraction of crude oil remaining in liquid state and the solid deposits. In the former, results indicate that the crude oil gets progressively heavier as it is heated up, even at the lower end of the temperature range where no solid deposits were observed in the MBR. The molecular weight distribution of the crude oil was found to increase upon heating showing the formation of larger molecules in the liquid, which may be related to deposit precursors. In the case of the deposits, it was found that their solubility properties are also different in several solvents in comparison with the original samples, which suggests that are chemical transformations accompanying there deposition. The amount of deposits obtained in each run has shown a strong dependence with temperature and residence time. No deposits were obtained at low residence times (1 hour) regardless of the temperature, which reinforces the role that stagnant zones in the heat exchangers have in the formation of deposits. Relatively high temperatures and long residence times favour deposition. The hypothesis that the only origin of the deposits was the asphaltene fraction of the crudes was put to test by carrying out fouling experiments in the MBR with the asphaltene-free heptane-soluble (HS) fraction of a crude oil (Venditti et al. 2009b). Carbonaceous deposits have been proven to appear not only from the asphaltene fraction of the crude, but also from this deasphalted crude. It was observed in some cases that the deasphalted fraction produced a larger amount of deposits than the crude oil itself under the same operating conditions. Work is ongoing to check these results with a broader range of crude oils as well as to analyse in more detail the chemical characteristics of both industrial and lab-scale deposits.

A new imaging technique based on infrared spectroscopy was applied to the characterisation of fouling deposits and asphaltenes. This attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopic imaging, which relies on the infrared focal plane array detector to simultaneously obtain thousands of spectra from different locations in a sample, is a non-destructive analytical technique and most importantly, provides both chemical and spatial information of a sample. ATR imaging spectrometers with a Focal Plane Array (FPA) detector are patented by Varian (Burka and Curbelo, 2000). The small penetration depth of the evanescence wave of the ATR approach makes it a convenient sampling method with little or no sample preparation and can be applied to highly absorbing materials such as carbonaceous hydrocarbons. The advantages and intrinsic limitations of ATR-FTIR spectroscopic measurements of high refractive index materials, such as petroleum deposits, have been addressed by Tay and Kazarian (2009). A lab-made aperture, developed by Chan et al. (2008), to vary the angle of incidence of the incoming infrared radiation in the ATR diamond accessory is used to correct the distortion of spectral bands due to the dispersion of refractive index. This allowed reliable spectral information to be obtained on high refractive index materials using ATR-FTIR spectroscopy with a diamond accessory. Tay and Kazarian (2009) introduce novel applications of combining macro and micro



Fig. 4 Macro ATR-FTIR images of deposits from a refinery PHT exchanger. Images show the distribution of a) CH stretching band, b) carbonate compounds, c) oxalate compounds and d) sulphate compounds.

ATR modes in FTIR imaging to characterise deposits from a refinery heat exchanger. Using different ATR accessories for the macro and micro modes, FTIR imaging yields important information about the spatial distribution of different components in the deposits. The macro ATR imaging approach provides a larger field of view which can be used to obtain the overall distribution of different components in the sample (Fig. 4). With the enhanced spatial resolution of the micro ATR approach, spectra of nearly pure components can be isolated. ATR-FTIR imaging allows the visualisation of different chemical components in a heterogeneous sample. Combining macro ATR and micro ATR-FTIR spectroscopic imaging, the complex petroleum deposit provides an important tool in chemical characterisation of fouling material which will aid in understanding the fundamental of crude oil fouling. Results demonstrate the viability of this approach; future in situ studies of heating of crude oil may reveal the onset of precipitation and deposition.

### **Sub-Project B: Interfacial and Rheological Properties**

The persistence of deposits on heat exchanger surfaces depends not only on the transfer of depositing material to the interface but also on the adhesion of this material to the surface. The adhesion of asphaltenic material onto surfaces will in turn depend on a number of complex factors including surface energies, surface temperature, the shear acting on the surface, and the nature of previously deposited layers (smooth, rough, dendritic etc.). Knowledge of the mechanical properties of the adsorbed asphaltene film is crucial if one aims to remove the film through mechanical or hydrodynamic forces. The aims of this subproject are: to charcacterise the interactions between asphaltenes and heat exchanger surfaces and to



Fig. 5 Determination of the interactions between an asphaltene coated glass particle and a stainless steel metal surface immersed in water at pH 5.5.

determine whether they can be reduced; to determine the interactions between asphaltene molecules and so provide data for the molecular modelling studies described under Sub-Project D; to determine the mechanical properties of the adsorbed asphaltene film, a necessary input into the modelling effort in Sub-Project C.

Atomic force microscopy (AFM) has been used to study the adsorption and adhesion of asphaltene to metal surfaces. Adhesion was monitored by attaching an asphaltene coated sphere to the AFM cantilever, pushing it against the metal surface, leaving it in contact for a certain period of time and then monitoring the force required to separate the metal surface from the asphaltene layer (Fig. 5). The interaction between asphaltene molecules was measured similarly, only with an asphaltene coated glass surface rather than a bare metal one. The local mechanical properties of the rheology of the asphaltene layer were determined by indenting a sphere into the asphaltene layer (the instrument was initially calibrated by indenting a film of cross linked polydimethylsiloxane, PDMS). Data were obtained both by compressing the films at a continuous rate (force measurement data) and by performing a stress relaxation experiment (any difference between the two methods is a consequence of some viscous flow of the film). The results are summarized in Table 1. All results obtained have been on asphaltene films deposited onto surfaces at room temperature. It is our hope that we shall be able to carry out similar experiments on asphaltene films deposited at the temperatures experience by heat exchanges, which will be supplied by Sub-Projects E and F.

Table 1 A summary of the mechanical properties of thin films of PDMS of 2 different cross link density, 10:1 and 10:2 and Maya asphaltenes.

	Young's Modulus (kPa)	
Material	Force Measurement	Stress-Relaxation
PS-PDMS 10:1	340	340
PS-PDMS 10:2	750	540
PS-Maya asphaltenes	1230	825

#### Sub-Project C: Fundamental transfer processes

The main aim of Sub-Project C is to achieve a detailed description of i) the fluid mechanics of the flow in the tubes of heat exchangers, ii) the heat and mass transfer associated with this flow and iii) their change as a function of temperature and deposition and removal inside the tubes. The ultimate goal is the development of mathematical and numerical tools based on first principles to predict, evaluate and minimize fouling in the tube-side of PHT exchangers.

The specific objectives of the sub-project are to develop capabilities to simulate accurately, reliably and efficiently the spatial-temporal evolution of the fouling process in the heat exchanger tubes as a function of the chemical, physical and thermal characteristics of the system. To this end, we have developed a mathematical model based on the conservation of mass, momentum and energy, which is complemented by a chemical equilibrium model based on the Gibbs free energy (Won, 1986, Svendsen, 1993). The latter is employed to account for the de-stabilization of organic components in the oil leading to phase separation. We also account for diffusion of the asphaltene phase to the pipe wall and its subsequent deposition on the wall in order to form the fouling deposit. The model also accounts for the changes in the physico-chemical, thermal and rheological characteristics of the deposit as a function of time due, for instance, to 'aging'-type phenomena. Finally, the model accounts for turbulent flow in the bulk, away from the wall, and can be extended to cover complex geometries. The predictions of the model are limited by the input into this model in terms of thermodynamic and physical properties. The reliability of the model predictions can therefore be enhanced with more accurate measurements of the latter, obtained in the other sub-projects of the CROF project.

We consider the dynamics of two immiscible materials undergoing pressure-driven flow in a cylindrical pipe or rectangular channel. These materials correspond to the crude oil and the foulant, located in the bulk and at the walls, respectively. The equations governing the flow in each phase are those of mass, momentum and energy conservation, which allow us to resolve the velocity, pressure and temperature fields in the oil and the deposit. Depending on the temperature and pressure distribution prevailing in the core, the chemical equilibrium model we employ allows the prediction of the amount of asphaltene that phase-separate and can diffuse towards and deposit at the walls. The governing equations are therefore strongly coupled by the physics of the deposition process. The oil is treated as an incompressible, Newtonian fluid, while the Coussot model (Coussot et al., 2006) is used to describe the time-dependent rheological characteristics of the deposit, which is also treated as incompressible. Numerical solutions of the governing equations are obtained subject to no-slip and no-penetration, and temperature conditions at the solid walls; constant flow rate conditions at the inlet, and outflow conditions at the outlet. Two approaches are used to solve the model equations depending on the nature of the flow regime in the tube. In the unrealistic but useful case wherein the flow remains laminar throughout, we use direct numerical simulations (DNS) of the governing equations; in cases where the flow is turbulent, we use large eddy simulations (LES). These approaches are described below.

Direct Numerical Simulations. Here, we use a diffuse interface method (DIM) formulation developed by Ding and Spelt (2007) and Ding et al. (2007), which has been suitably modified to account for fouling deposition and the 'aging' phenomena described above. The DIM formulation allows one to trace the interface between the two phases (oil and deposit) and can accommodate the changes of topology that will accompany the displacement and entrainment of the deposit following its interaction with the bulk flow of oil. Use of the DIM formulation (as opposed to the LES approach described below) also affords one the opportunity to elucidate the physics of the interaction of the two phases and the aging phenomena (Coussot, 2007) in the absence of the complexities associated with the presence of turbulence. The understanding gained as part of this approach provides an input into the LES studies. Sample results are shown in Fig. 6 starting from an initially thin, fouling layer at the wall of uniform thickness. Here, it is clearly seen that the interaction between the oil and deposit phase leads to the development of interfacial waves. In the absence of aging and deposition, this interaction results in the removal of the deposit (Fig. 6a); in the presence of these effects, however, the deposit persists (Fig. 6b).

Large Eddy Simulations. In order to carry out LES, the commercially-available code ANSYS CFX was employed. This code utilises the Volume of Fluid method and allows the inclusion of turbulence models and complex geometries in the flow simulations; this, then, permits simulation of the realistic case of a heat exchanger tube-side. In the present work, we account for deposition and aging processes in cylindrical pipe geometry. The dynamics accompanying the turbulent oil flow are now considerably more complex than those associated with the laminar flow shown in Fig. 6. Simulation results clearly show the waviness of the interface separating the two phases, as well as the removal of the deposit and its entrainment into the bulk oil phase, promoted by the turbulent flow.

For future work, we aim to use the models developed so far to carry out parametric studies of the fouling process in order to elucidate its dependence on the relevant system parameters. Of particular interest would be the determination of the variation of the pressure drop and the total mass of foulant deposited on the walls as a function of time, and the implementation of measures that would mitigate against fouling-induced pipe blockage.



Fig. 6 DIM simulations of fouling in the absence and presence of deposition (a) and aging (b). The initial, intermediate and late-time dynamics are shown in the top, middle and bottom panels, respectively Details can be found in (Sileri *et al.* 2009).

### Sub-Project D: Thermodynamics and molecular modelling.

The objectives of Sub-Project D are (i) to develop a molecular model of asphaltenes in the context of physicallybased equation of state and (ii) to exploit the link between the equation of state and the underlying intermolecular potential to perform molecular simulations on asphaltenecrude systems. We have taken the task of utilizing macroscopic information regarding experimental asphaltene deposition boundaries and developed a thermodynamic model based on a molecular-based equation of state (EoS). A recent implementation of the Statistical Associating Fluid Theory (SAFT) (Gil-Villegas et al., 1997) is used, (for a review of SAFT and its applications see Müller and Gubbins, 2001) and by appropriately adjusting the intermolecular potential parameters to capture the data we obtain effective coarse-grained parameters that represent in an average way a potential of model asphaltene-like fluids. This latter molecular description allows us to perform molecular-dynamics (MD) simulations to obtain the details of the aggregation mechanisms on a microscopic scale.

In this particular application, there is much uncertainty in the exact molecular description of asphaltenes (see for example Aguilera-Mercado et al., 2006, for a discussion on the archipelago and continental models for asphaltenes) so we model the system initially as an asymmetric binary mixture consisting of a polymer (polystyrene) in oil (hydrocarbon). We have shown, in the context of this project, how this Polystyrene Asphaltene Mapping (PAM) can be used to describe phase behaviour of asphaltene deposition. Fig. 7, our calculated pressure-temperature projection of the mixture phase diagrams for asphaltene + oils of different molecular weights, exemplifies the method. We model the system of Buenrostro et al., (2004) using a PAM of molecular weight 3066 g mol<sup>-1</sup> to represent the asphaltene together with a  $C_9$  oil. The black squares represent the asphaltene precipitation data from Buenrostro et al. (2004); the connected symbols represent our calculations. Areas under the curves represent states where phase separation occurs. It is seen that the PAM model is consistent with the experimental data. In addition, we predict the effect on the phase diagram of altering the molecular weight of the oil (e.g., by adding heavies or lights). As expected, the lighter the oil (solvent) the larger the region of immiscibility for the asphaltene. Furthermore, the model predicts that at constant pressure, one may, given the correct conditions, observe a two phase split of an otherwise homogeneous fluid upon an increase in temperature. This latter phenomena is seen in experimental data for asphaltene precipitation, but is rarely captured by conventional thermodynamics modelling. The PAM model is straightforward to apply, given the knowledge of some experimental data from which to infer the analog fluid.

Although other EoS can be used to model asphaltenedeposition behaviour, the parameters in these EoS cannot be traced back to intermolecular potentials. The SAFT model, on the other hand, is based on a rigorous statisticalmechanical theory, so the parameters may be used in molecular-modelling studies. We have performed large-



Fig. 7 Pressure-temperature projection of the phase diagrams of mixtures of asphaltene  $(MW = 3066 \text{ g mol}^{-1})$  with oils of increasing molecular weight.

scale MD simulations of archipelago-like molecules and more conventional continental-like models with the parameters obtained using PAM models and have obtained the expected qualitative behavior. Having a well defined molecular model that represents in a broad sense the molecular detailed behaviour of asphaltenes and crudes will allow us in the future to explore other fundamental issues such as: aggregation rates and tendencies, the effects of interfaces on the precipitation of asphaltenes. Furthermore, moelcular modelling allows clear visualization of the underlying molecular physics leading to the macroscopic behaviour.

### Sub-Project E: Stirred Vessel Fouling Tests

The objectives of Sub-Project E are (i) to design and operate a small high pressure, high temperature stirred cell ( $\approx$  1 litre oil volume) based on the Eaton patent (1983) and the ensuing Eaton and Lux paper (1984), (ii) to obtain fouling rate data as a function of both temperature and surface shear stress for a range of crude oils of interest to the CROF partnership, (iii) to interpret the data using established and new models of fouling behaviour, (iv) to characterize deposits, deposit distributions and thicknesses, (v) to supply samples of deposits and crude oil to other partners for further specialist characterization at Imperial College, (vi) to compare experimental data with that obtained from the continuous flow loop apparatus at Imperial College, and (vii) to integrate information, data and models from the batch cell experiments into the overall CROF project.

Fig. 8 shows the general arrangement of the batch stirred cell which has been constructed from a steel block. The cell has been designed to operate at a crude oil bulk temperature and pressure up to 300 °C and 30 bar, respectively. The crude oil is agitated by a rotating concentric cylinder placed around the central electrically heated test finger which has been designed to operate with a surface temperature over 400 °C, if required. The cell is designed principally to obtain experimental data for



Fig. 8 Batch stirred vessel based on the Eaton and Lux design (Young *et al.*, 2009).

operating conditions which are typical of the hottest parts of the crude oil preheat train. The agitator is driven through the top flange by an electric motor which is fitted with a magnetic drive unit. The batch cell is fitted with a crude oil bulk temperature thermocouple and a cooling coil through which a non-fouling heat transfer oil is passed. Heat is ultimately dissipated to atmosphere.

The test finger is heated internally by a cartridge heater, the heat flux from which is controlled electrically. Three thermocouples are inserted at various heights inside the wall of the test finger. Being operated at constant heat flux and constant bulk crude oil temperature, the rate of fouling becomes equal to the rate of change of test finger wall temperature with time. The test finger/cartridge heater assembly can be removed from the base of the batch cell so that the test finger can be removed for inspection and deposit characterization. An example of a deposit on a test finger is shown in Fig. 9. The distribution of the deposit thickness along and around the test finger is made by a laser and coherent light scanning procedure (Proscan). SEM and close-up photography support the morphological analyses. The experimental data are supported by CFD analysis using COMSOL (Yang et al., 2009a). CFD provides not only the flow patterns in the batch stirred cell but also predictions of the distributions of surface temperature and surface shear stress. These predicted distributions are validated against experimental data. CFD has revealed (i) that the surface shear stress is virtually constant along the axial length of the test finger, except at it ends, and (ii) that there is a near parabolic distribution of surface temperature along the length of the test finger.

Large quantities of experimental data have been generated with three different crude oils (Young *et al.*, 2009). In virtually all cases the fouling rate has been found to be constant beyond the induction period. An induction period is not usually found for an imperfectly cleaned test

finger and this is in accordance with induction period modeling (Yang *et al.*, 2009b). Experiments can be completed during one day (< 10 hours) if required, and it has been found that they can be continued from day to day if necessary with an overnight shut-down revealing no loss of continuity in the fouling curves. Some examples are detailed in a paper at this conference (Young *et al.*, 2009).

Achievements to date have included (i) the accumulation of crude oil fouling data as a function of surface temperature, bulk temperature and surface shear stress for three crude oils, (ii) the calculation of Arrhenius data confirming that apparent activation energies are a function of surface shear stress (Crittenden et al., 2009), (iii) the creation of compensation plots (Crittenden et al., 2009) for the new experimental data alongside previous data on crude oils, inorganic salts and proteins, (iv) the extrapolation of data in order to obtain threshold fouling temperatures for given surface shear stresses, giving rise to the ability to test existing threshold fouling models (e.g. Ebert and Panchal, 1997), and (v) the creation of an induction period model which has been tested on new and existing crude oil data as well as on inorganic and protein fouling (Yang et al., 2009b).

The batch stirred test cell is relatively fast to use. Not only can crude oil samples can be changed relatively quickly but also a considerable amount of experimental data relating to the effects of bulk temperature, surface temperature and surface shear stress can be obtained typically within one day. The ex situ techniques of surface profiling and CFD (Yang et al., 2009a) add a considerable amount of complementary and verification data. Both the starting and final chemistries have been studied in order to ascertain whether there have been any significant changes that might have an impact on both the fouling propensity and the induction period. Parameters focused on have been asphaltene precursor concentrations together with material and surface properties (Young et al., 2009). Experimental fouling rate data can be obtained directly from changes in the three test finger thermocouples knowing the local heat flux. Since the fouling rate is constant with time, the change of the rate of fouling as a function of surface temperature can be found at the end of an experimental run when the deposit thickness has been measured using the Proscan technique. The rate of increase in fouling deposit thickness can be correlated against the CFD predicted surface temperature to provide a continuous Arrhenius plot along the length of the heated test finger. This means that, for the first time for crude oils, a single fouling experiment has



Fig. 9 Typical deposit on a mild steel test finger (Yang *et al.*, 2009a) (finger is vertical in the apparatus).

been used to obtain the Arrhenius parameters which can then be incorporated into the compensation plot analysis (Yang *et al.*, 2009a). A new generic lumped parameter model of fouling with an induction period has been developed (Yang *et al.*, 2009b). The new model can be used to fit experimental data from the start of the induction period through to the fouling growth phase. Two different types of crude oil have been studied.

Future work will focus particularly on developing and testing models for crude oil fouling as a function of process conditions, including induction periods, fouling thresholds and compensation plots. Experimental work will continue on providing data, information and samples to other partners, broadening the ranges of crude oils and operating conditions. We plan to determine comparability between fouling data obtained using the batch stirred cell with those from the continuous flow loop. Finally, it is planned to study the effects of metallurgies, surface finishes and intensification devices on crude oil fouling rates.

### Sub-Project F: Annulus Flow Tests

The design, construction and operation of a high temperature, high pressure, crude oil flow loop equipped with electrically heated test sections on which deposits will form was undertaken at Imperial College London in collaboration with the University of Cambridge. The loop will be used primarily to study the effects of fouling on heat transfer and pressure drop in an annulus test a shell-and-tube heat section, simulating flow in exchanger. The rig will also accommodate analysis within an actual size exchanger tube and could, in the future, be used to study fouling in more complex heat exchanger geometries. The system thus permits comparison between tubular, annular and possibly other geometries. The annulus configuration has been used in previous laboratory investigations, e.g. the HTRI heated rod system, and allows fouling deposits to be recovered or imaged in situ.

The rig configuration will permit the continuous monitoring of the heat transfer rate between the electrically heated test section surface and the flowing crude oil, hence inferring the rate of build-up of fouling resistance. This will be achieved by accurate monitoring of the inner surface temperature of the heated annulus test section, using a radiation equilibrium thermometer. The actual thickness of the foulant layer will be measured simultaneously using a novel dynamic gauging technique developed at the University of Cambridge. The pressure drop though the test section will also be measured continuously, as further evidence of build-up of the foulant layer. Fouling rate data will be compared with data derived from the stirred vessel tests being conducted at the University of Bath (SP-E) and from refinery heat exchangers, with the hope of detecting systematic linkage between fouling rates. Furthermore, samples of deposits will be recovered from the rig for chemical/rheological characterisation, as a function of position, time, flow conditions, oil type etc., in Sub-Projects A and B. The rig will also provide the facility, in combination with group G, for testing of fouling control and mitigation strategies, such as surface modification; the use



Fig. 10 Flowsheet for the fouling flow loop.

of crude oil anti-fouling additives; and cleaning strategies. The flow loop has been designed to supply crude oil to the heated test section at a maximum temperature of 300 °C, although initial operations will be limited to 200 - 270 °C.

The maximum loop operating pressure is 30 bar<sub>g</sub>. The annulus test section is 2 m long, permitting fouling measurements over about 1.5 m, after allowance for an entry section for flow stabilization. The optimal oil delivery configuration (4 injection points) was identified from CFD studies. The inner tube will be subject to direct electrical resistance (Joule) heating. Test surface temperatures of 250 – 350 °C are planned, i.e. oil plus 120 °C maximum, leading to an imparted heat flux from the surface to the oil in the region 20 – 100 kW m<sup>-2</sup>. Fluid hydrodynamics will be representative of conditions in refinery shell-and-tube heat exchangers, with a linear velocity in the region 1 – 3 m/s, and Reynolds number up to a maximum of 20,000. A standard tubular test section will be mounted in parallel to the annulus section.

A schematic diagram of the complete flow loop is given in Fig. 10 and a photo is shown in Fig. 11. The test section, which is connected to power supplies capable of delivering up to 20 kW, is equipped with a radiation equilibrium thermocouple (Bennett et al., 1961) inside the inner tube and a fluid dynamic gauge within the annular gap. The thermocouple, contained within ceramic shields, traverses axially down the test section and measures the temperature of the inner wall of the heated tube to a high degree of accuracy. The temperature of the outer wall, on which deposition is occurring, can be calculated exactly from this measured inner wall temperature, plus the electrical power supply, by consideration of the radial conduction through the cylindrical tube wall (Barbosa, 2001). The outer wall temperature will fluctuate, at a given power input and oil flowrate and inlet temperature, in response to build-up of the fouling layer on the tube outer surface. Combination of the heat transfer and the dynamic gauging measurements will permit direct estimation of the thermal conductivity of the fouling layer for the first time. The pressure gradient will be measured using high temperature pressure transducers. Since the surface of the deposit will be rough and the outer tube relatively smooth, the shear stress on the inner surface will be calculated from the pressure gradient using a



Fig. 11 Side view of the fouling flow loop.

transformation method (Hewitt, 1964).

Fluid dynamic gauging (FDG), a non-contact technique developed at Cambridge, allows the thickness of soft solid layers to be monitored in situ and in real time. An account of the FDG technique is given in Tuladhar et al. (2002). The device works by measuring the flow rate of liquid through a nozzle located close to, but not touching, the surface. This separation distance, or clearance, h, changes as a deposit grows or is removed: it is tracked over time to yield thickness-time profiles. FDG had not been applied to curved surfaces before, nor at the operating pressures and temperatures planned for the test loop. A cold flow system was constructed at Cambridge, replicating the test loop geometry, and demonstrated that FDG can be applied to annular surfaces across a wide range of flow rates. Results show that the mass flow rate-clearance profiles exhibit the sensitivity to  $h/d_t$  required to locate the deposit surface under the turbulent flow conditions expected in the fouling test section experiments. The paper by Gu et al. (2009a) presented at this conference reports extension of the work to lower Reynolds numbers and to heated surfaces, in particular a heated rod system similar to the HTRI probe. They demonstrate the successful application of FDG to track the growth of a soft simulated milk fouling deposit. They also report computational fluid dynamics (CFD) simulations of the gauging system at low annulus Reynolds numbers, which allows the stresses being imposed on the surface under study to be quantified. This information can be used to characterise the strength of the fouling layer. These studies have enabled an FDG system to be designed for service in the Imperial College test loop. This incorporates a new mode of FDG operation, intended to minimise disruption of the flow field and fouling layer during gauging. Thickness measurements are made intermittently, and disruption of the fouling layer checked by comparing local measurements of the surface temperature using the travelling radiation thermocouple.

The rig is designed to be operated remotely and the control system incorporates automatic shut-down procedures

in the event of the detection of any mal-operation. Continuous running periods of 2-5 days are envisaged, based on estimates of fouling build-up using the well known Ebert-Panchal correlation.

At the time of writing (April 2009), construction of the flow loop and its containment has been completed and manufacture of both the annular test section and the dynamic gauge is well under way. Commissioning of the system will commence shortly, using Paratherm in the first instance. The first fouling tests are planned for Autumn 2009 and will be conducted using a post-desalter crude blend supplied by Petronas of Malaysia. Small samples of this blend, plus its constituent crudes, are being studied elsewhere in the CROF project.

### Sub-Project G: Control and mitigation

Activities here concentrated on developing tools and techniques for scaling up the results and models generated in the detailed investigations for application to refinery exchangers and units, particularly the networks of exchangers found in crude distillation unit preheat trains. The work was sub-divided into two parts (Fig. 12). The main focus of Part A was the construction a new modelling platform which could simulate the impact of fouling on the performance of an individual heat exchanger. This required the local fouling rate and deposit thickness to be evaluated over time and space (i.e. across all points in the exchanger), and designed so that it could incorporate the models developed by the fundamental investigations. The overall performance of the exchanger could then be evaluated and expressed in terms readily understood by operators such as the overall fouling resistance and the pressure drop across the unit. The importance of parameters in the detailed fundamental models could thus be established, and those critical for unit performance identified. Such models, although still detailed, are rather "simpler" than those developed in Sub-Project C, and are essential for network simulations, as the more complex models can both render the problem difficult to solve (or require enormous effort).

The platform was constructed using the 'threshold fouling' model of Ebert and Panchal (as reported by Polley *et al.* 2002) for fouling calculations and implemented in the gPROMS simulation environment (Process Systems Enterprise, 1997-2009). The single exchanger model was validated against actual plant data in a demanding hot-end exchanger (Coletti and Macchietto 2009a) showing excellent predictive capabilities. Multiple exchangers in a network could then also be readily simulated (Coletti and Macchietto, 2009b) to give a detailed quantitative



Fig. 12 Schematic of simulation activities, linking scientific advances to plant operations



Fig. 13 Cumulative costs of fouling over 1 year after cleaning (Coletti and Macchietto, 2009b).

assessment of the costs of fouling (Fig. 13).

Part B considered the effect of fouling on the thermal and hydraulic performance of preheat train networks. It was decided to focus on existing networks, and thus on the operation and retrofit of existing systems rather than the design of new units, as this was a greater priority for operators. Design must include the distillation system, and represents an area for further work. A network simulation tool was constructed in the MATLAB programming language combining the preheat simulation approaches developed by Wilson et al. (2001) and the exchanger modelling methods reported by Yeap et al. (2004). The simulation incorporated crude flow rate variation caused by high pressure drop, cleaning, and varying fouling rates in individual exchangers calculated using threshold fouling models. Similarly to Part A, the tool was constructed so that more advanced fouling models could be 'plugged in' once they became available.

In modelling the performance of a network subject to fouling, and including realistic operating features, the simulation tool allows different mitigation options to be compared (and fouling managed) on the basis of quantitative indicators. The paper by Ishiyama *et al.* (2009a) illustrates the importance of management parameters (cleaning, fuel and production costs) on optimal cleaning (and noncleaning) decisions. Simpler optimisation methods were employed, deliberately, to calculate cleaning schedules in order to retain the engineering insight to the problem. Their paper at this conference (Ishiyama *et al.* 2009b) reports application of the simulation to an operating refinery, including control of key internal variables such as desalter temperature. Future work will include development of a refinery software tool and extension to design aspects.

Existing models such as the 'threshold fouling' approach do not incorporate deposit ageing, which could be important in extending experimental results and models to heat exchanger performance. There has been little quantitative work on this aspect of chemical reaction fouling and a new modelling framework for ageing was developed as part of this work (see Ishiyama *et al.*, 2009c).

### Sub-Project H: Technology transfer

The promotion and coordination of interactions with

industrial partners within CROF is carried out by IHS ESDU of London, represented by its Director of Process Engineering Technology. ESDU has a long tradition of brokering industrial innovation. It produces, under the guidance of independent expert, industrially-based committees, high-quality engineering data and software for industry and the Universities. ESDU has been working on fouling since the mid-1980's, with particular emphasis in the last five years on crude oil fouling.

The CROF project evolved from the collaborative efforts of the oil industry companies that form the IHS ESDU Oil Industry Fouling Working Party. This Working Party, representing some 70% of the world's refining capacity, was formed in 1999 in recognition of both the economic importance of crude oil fouling and acceptance that oil companies working with each other and with leading international researchers in the field was the best chance to find practical methods of fouling abatement.

In 1999 there was a landscape of very low oil prices -US\$10/bbl - and very low refinery margins. Although the economic landscape has changed considerably in recent years and even months, refinery margins remain very tight and the importance of fouling abatement is even more acute. For example, the environmental effects of burning excess fuel is now being recognised in legislation, with refineries looking to minimise CO2 emissions and operate as efficiently as possible and minimize use of their carbon emissions credits. Oil refining is an extremely safetyconscious industry, and safety problems associated with the disposal of toxic fouling waste products and over-frequent maintenance operations have to be minimized as far as is practical. Tools developed by IHS ESDU with this Working Party, and especially the heat exchanger analysis program EXPRESSplus, are now being applied by the oil company members of the Working Party. However, within this group it was recognized that to make a real step-change in understanding the nature of fouling problems it was necessary for strategic funding for the coordinated project that is CROF.

As technology transfer partner for the CROF project, IHS ESDU bridges the gap between industry and research and facilitates close cooperation between all parties. It organized bi-annual research and development meetings taking place at various locations in the UK, including an IHS ESDU office, Imperial College, Cambridge University and, most recently (April 2009) the Chevron refinery in South Wales. As an example of the commitment of the refiners to the CROF project, engineers travelled from four continents to attend the 3 day meeting kindly hosted by Chevron which welcomed over 40 engineers and scientists, followed by lab visits to Bath and Imperial College.

Early in the project, the main concern was exchange of information and advice on setting the research directions. As the experimental programme started, access to representative crude oil samples became a key issue and adequate quantities of crude were supplied from around the world. More recently, a number of industrial case studies were set up providing access to valuable plant data and personnel. Some of the case studies have already been completed and are providing invaluable assessment of the techniques under development, feedback from operations and a measure of their potential eventual impact.

### CONCLUSIONS

The project presented represents possibly the largest combined academic/industrial effort towards the systematic understanding and solution of oil fouling problems in several decades. So has the problem been solved yet? The simple answer is not yet, however results so far indicate the interdisciplinary, multiscale, combined experimental and theoretical, industrial and academic approach of CROF is very powerful and that excellent progress has been achieved in a relatively short time.

A team has been created which brings together most of the skills required. Exchanges between researchers across the various sub-projects are fostered by regular meetings between the researchers, with regular presentations of respective results, questions and answer session, and by many more informal sessions. Progress reports from each subgroup are circulated to all researchers and there is a common repository of data, information, reports, papers, etc through a project website, with private and public sections. It is very clear to all involved that this has led to very significant progress in developing an understanding of the overall problem and the potential of each other's techniques to address its various angles. In several cases this new understanding has brought about a re-orientation of the scientific work in much more tailored directions, which reinforce and complement each other's work.

Excellent experimental facilities have been designed and built which are starting to provide data of quality and range not previously available. Progress in the characterization of deposits has also been significant. In particular, the ability to generate and collect fouling deposit samples in controlled conditions and to deploy a number of complementary analysis techniques, including some on-line ones, on the same samples opens a new window of rich primary information. Modelling at the molecular-scale level of transport and thermodynamics is hard work, but again significant progress is being made with simplified "model" systems which however seem to offer good representative features. At the industrial equipment unit scale, progress has been made in devising rather more detailed, distributed models than used in the past for heat exchangers which can incorporate a variety of deposition, heat transfer and deposit ageing processes. The "threshold fouling" approach (used in this context while awaiting for the new thermodynamics, transport and reaction models from the other groups) has been given a significant extension. Work at the exchanger network scale has produced a new way to incorporate fouling when devising cleaning scheduling.

There is obviously much left to do, and in many ways, things are just warming up. Some future activities have been indicated above in the description of the work of each of the groups. The main future opportunity however will lie in exploiting the interaction between quality experimental data, which are now becoming available, and theoretical modeling work at all levels, for the purpose of parameter estimation, testing and validation. There will also be the need, and opportunity, to more closely integrate the results of the various groups. A specific outcome of the close exchanges within CROF has been a new awareness of how the results of a group need to be "packaged" in order for others to use them, which data are needed and in which form. This bodes well for such integration effort. Finally, the need continues for pilot scale and plant "case studies" to validate all work, in collaboration with the industrial partners of the project. Supported by such validation efforts, there will then be the opportunity to use the new machinery to address mitigation strategies via improved operations and new heat exchanger design methodology.

Feedback on the CROF work and project so far has been excellent, and the initial three years were extended to the end of 2009. There is a strong industry demand and support for the project to continue and the team to be kept together. To this effect, a proposal is under way (April 2009) to consolidate the present project into a more permanent interdisciplinary Centre for research on fouling and cleaning. It is envisaged its scope will be extended to cover a number of related application areas: crude oil preheat trains (building on the work in CROF); upstream (heavy) oil recovery to include fouling within reservoirs due to asphaltene and wax deposition during production; water cooling systems (including scale formation, bio-fouling and particulate fouling), food production systems; production of biomass-based fuels; nuclear and conventional power production systems. All these problems share several generic features that include the poorly understood mechanics, thermodynamics and physical chemistry of deposition and removal, and will benefit from a combined experimental, theoretical, mathematical modelling and systems engineering approach.

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