Energy Efficient Heat Exchange and Catalysis
The UNIHEAT Project

Dr. Francesco Coletti
Industry Engagement Manger

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Overview

- Energy efficiency in thermal and catalytic processes
- Overview of the UNIHEAT project
- UNIHEAT Research programme
  - Crude oil fouling
  - Other UNIHEAT research themes
- UNIHEAT Industry Engagement Programme
Energy demand & utilisation

Growing global energy demand

Energy utilisation

Energy efficiency plays a key role in meeting demand
Thermal energy efficiency

Industrial energy consumption in the UK (2013)

72% of energy is consumed in thermal processes
Thermal energy efficiency

Technical energy saving potential in the chemical industry

Global thermal savings in chemical processes > UK total E consumption!

Note: Energy savings potential based on 2010 production levels.
Source: IEA.
Savings potential via catalysis

Data for chemical industry
Source: DECHEMA

Large opportunities by improved catalysis and catalytic processes
Energy in oil refineries

Oil Refineries ~ 5-7% of crude oil energy to operate

- **Current** average energy used
- **Practical minimum** energy
- **Theoretical minimum** energy required

Over 25% of refinery energy losses could be practically recovered

(Source: US DOE, 2006)
UNIHEAT Project - Overview
The numbers

US$ 15 Million project funding

3 year programme

71 research team members

A target of 8 patents

Largest research project ever assembled in this area
Project objectives

Radical increase in industrial energy efficiency

Target industries: oil and gas, in particular refining, petrochemicals and power

• Improving design of heat exchange equipment, energy recovery networks
• Intensification of heat exchanging processes by preventing fouling
• Reduction of hydraulic drag in oil pipelines
• Recovery and efficient utilisation of waste heat
• Advanced modelling for efficient management of combined heat and reaction in oil and chemical processes utilising new catalysts
• Enhancing energy efficiency in catalytic processes for the petrochemical industry
• Improving industrial processes for heavy oil upgrading
• 3,000 academic and research staff
• 15,600 students
  – (>1/3 postgraduate)
  – 126 countries
  – 49% Full time students non-UK nationals
• £765M turnover (£314M Research)
• Technology transfer:
  Imperial Innovations
  – 555 Patents filed
  – 150 Licences under management
  – £120 million Invested in spinouts since 2006
  – £370 million Raised by spinouts since 2006
  Imperial Consultants
  – Leading UK academic consultancy provider
  – 500+ Imperial staff involved
  – Annual turnover >£20m
  – Wholly-owned subsidiary of Imperial College
Boreskov Institute of Catalysis - BIC

Founded by
G.K. Boreskov (1958-1984)
One of the largest R&D centres in catalysis
Developed > 75 catalysts and catalytic tech.
Highly-skilled personnel:
  – 1300 staff
  – 400 researchers
  – 5 members of the Russian Academy of Sciences
Advanced catalysts and nanomaterials preparation
Pilot plant facilities

Catalysts & catalytic processes
- Conversion of light hydrocarbons & natural gas
- Oil refinery, heavy oil
- Key processes of chemical industry
- Natural gas treatment (desulfurization, etc.)
- Pharmaceutics
- Agricultural chemistry
- Polymerization of olefins
- Porous oxides
- Zeolites
- Environmental protection
- Non-traditional energetics, utilization and conversion of renewable feedstocks and coal

Adsorbents and composite materials with adjustable properties
- Selective sorbents of $\text{H}_2\text{O}$, $\text{CO}_2$ etc.
- Carbonaceous materials and technical carbon
- Fillers on the base of disperse materials
**Structure**

**Funding**
- Skolkovo resident company - Applied Research Centre
- "Energy Efficient Heat Exchange and Catalysis"
- Steering committee
  - 2 directors

**Research Programme**
- Principal investigators
- Shared, pre-competitive research

**Industry Engagement Programme Manager**
- Proofs of concept

**Other UNICAT activities**
- UNIHEAT Industrial projects
- Individual Partners
  - Confidential, separate contracts
- Industrial demonstrations
  - Feasibility studies

**Agreement open for more Partners to join**

Credits: Prof. S. Macchietto
UNIHEAT Project - Research programme

- Crude oil fouling
- Other UNIHEAT research themes
The UNIHEAT research team

<table>
<thead>
<tr>
<th>Name</th>
<th>Affiliation</th>
<th>Area of Expertise/Role</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prof. G.F. Hewitt</td>
<td>Imperial College London</td>
<td>Heat transfer, multiphase flow, nuclear power</td>
</tr>
<tr>
<td>Prof. G. Jackson</td>
<td>Imperial College London</td>
<td>Thermodynamics</td>
</tr>
<tr>
<td>Prof. S. Kazarian</td>
<td>Imperial College London</td>
<td>Advanced spectroscopic imaging, supercritical fluids processing</td>
</tr>
<tr>
<td>Prof. V.A. Kirillov</td>
<td>Boreskov Institute of Catalysis</td>
<td>Chemical engineering, heat and mass transfer, catalytic combustion</td>
</tr>
<tr>
<td>Prof. O.K. Matar</td>
<td>Imperial College London</td>
<td>Interfacial fluid mechanics, multiphase flow, first principle modelling</td>
</tr>
<tr>
<td>Prof. S. Macchietto</td>
<td>Imperial College London</td>
<td>Process Systems Engineering, UNIHEAT project co-director</td>
</tr>
<tr>
<td>Dr. C.N. Markides</td>
<td>Imperial College London</td>
<td>Heat transfer, thermodynamic cycles, energy conversion</td>
</tr>
<tr>
<td>Prof. O.N. Martyanov</td>
<td>Boreskov Institute of Catalysis</td>
<td>Catalysts and nanostructured materials physicochemical characterization, supercritical fluids , UNIHEAT project co-director</td>
</tr>
<tr>
<td>Dr. M. Millan-Agorio</td>
<td>Imperial College London</td>
<td>Catalytic upgrading of heavy oil, analytic characterization techniques</td>
</tr>
<tr>
<td>Prof. E. Müller</td>
<td>Boreskov Institute of Catalysis</td>
<td>Thermodynamics, Molecular simulation</td>
</tr>
<tr>
<td>Dr. A.V. Porsin</td>
<td>Boreskov Institute of Catalysis</td>
<td>Catalysts for air purification and fuel combustion, design of catalytic reactors, development of methods for testing catalysts and reactors</td>
</tr>
<tr>
<td>Dr. V.N. Snytnikov</td>
<td>Boreskov Institute of Catalysis</td>
<td>Catalysis, mathematical modelling, parallel algorithms, spectroscopy, chemical evolution, computational mathematics</td>
</tr>
<tr>
<td>Dr. V.A. Yakovlev</td>
<td>Boreskov Institute of Catalysis</td>
<td>Biofuels, hydrotreatment catalyst, combustion in FCB</td>
</tr>
</tbody>
</table>

+ 28 Students, 22 Research associates, 2 technicians
From molecular to plant scale

- **Chemical Characterisation of oil and deposits**: 2, 10, 11
- **Thermodynamics & molecular modelling**: 4
- **Experimental Measurements**: 1, 9, 10, 11, 12
- **Heat exchange and pipeline equipment design**: 6, 10
- **Heat & Reaction management Reactor design**: 6, 8, 9, 12
- **Integration Plant data analysis Energy recovery networks Efficiency Optimisation**: 6, 7, 8, 9
- **Physical Characterisation of oil and deposits**: 3, 11
- **Catalytic processes**: 8, 10, 12
- **Rheological and transfer processes**: 5, 9, 10
- **Kinetics modelling and validation**: 6, 9
- **Waste Heat Recovery and conversion**: 7, 8, 12

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### Equipment Unit

- **Heat & Reaction management Reactor design**: 6, 8, 9, 12
- **Heat exchange and pipeline equipment design**: 6, 10
- **Integration Plant data analysis Energy recovery networks Efficiency Optimisation**: 6, 7, 8, 9

### Plant

- **Heat & Reaction management Reactor design**: 6, 8, 9, 12
- **Heat exchange and pipeline equipment design**: 6, 10
- **Integration Plant data analysis Energy recovery networks Efficiency Optimisation**: 6, 7, 8, 9

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**Molecular**

**Pilot Plant**

**Equipment Unit**

**Plant**
The UNIHEAT themes

1. Multi-scale modelling of crude oil fouling: from molecular to plant scale

2. Physico-chemical properties of oil and deposits

3. Heavy Oil Catalytic Upgrading

4. Thermodynamic power generation cycles for improved efficiency

5. Drag reduction in pipelines

6. Thermodynamics: Equation of state & molecular modelling of heavy oils

7. Oil fouling tests in HIPOR facility

8. Laser induced ethane pyrolysis
Crude oil fouling

1. Multi-scale modelling of crude oil fouling: from molecular to plant scale

2. Physico-chemical properties of oil and deposits

6. Thermodynamics: Equation of state & molecular modelling of heavy oils

7. Oil fouling tests in HIPOR facility
UNIHEAT Project - Research programme

- Crude oil fouling
- Other UNIHEAT research themes
Crude Distillation Unit

Heat transfer ↓
Pressure drop ↑

Top pump around

25 ºC Kerosene

Storage

Desalter

Heavy gas oil

Light gas oil

Bottom pump around

Kerosene

Furnace

300 ºC 570 ºF

360 ºC 660 ºF

Bottom pump around

Reduced crude

Fuel ↑

Kerosene

Light gas oil

Heavy gas oil

Reduced crude

Coil Inlet Temperature ↓
Throughput ↓
Impact of fouling (100,000 bbl/day) $11,000,000 p.a.

Reduced heat transfer
- Additional surface area $75,000 per unit
- Stand-by heat exchangers
- Dosing equipment for chemical additives
  - Chemical additives $350,000 p.a.
  - Throughput reduction (Production loss): $8,500,000 p.a.

Excessive Pressure drops
- Increased equipment corrosion
- Cleaning $50,000 per unit
- Increased electricity for extra pumping
- Production loss during shut-down
- Out of spec after shut-down

Economics
- Running costs: Capital costs
- Losses
- Operations
- Additional furnace fuel: 1°C drop in CIT = $500,000 p.a.
- Extra emissions 1°C in CIT = 1 ton/day CO2
- Chemical additives
- Waste disposal (carbonaceous material with sulphur, Nitrogen and metals)
- Crane operations
- Personnel Health & safety

Environment
- Extra emissions
- Waste disposal

Safety
- Crane operations
- Personnel Health & safety

Image courtesy of Hexxcell Ltd.
Fouling in pictures

Photo courtesy Prof. Crittenden
Cleaning

Photo courtesy Prof. Crittenden
Ask this guy!
Crude oil fouling - challenges

- Measure
  - New experimental techniques
    - Small & large scale
- Understand
  - Oil & deposit characterisation
  - Deposition kinetics
  - Interfacial/rheological properties
  - Thermodynamics and molecular properties
- Model
  - At all scales, dynamics
  - Integrate
  - Validate
  - Scale up
- Mitigate/Improve/Optimise
  - Process
  - Exchanger design/retrofit
  - Energy integration networks
  - Control and operations

Crude oil fouling – UNIHEAT

Experimental

Fouling deposit analysis

Signal (Norm.)

Retention time (min.)

Size Exclusion Chromatography

Increasing molecular size

Molecular & Thermodynamic

Fundamental transport phenomena

Modelling

Industrial scale

Crude oil characterization

Chemical Imaging

X-ray scattering

Fouling rigs

Crude B Fresh Crude Oil
Heated Crude 200
Heated Crude 280
Heated Crude 390

Increasing molecular size

Crude oil characterization

Fundamental transport phenomena

Industrial scale
Crude oil fouling – modelling

UNIHEAT Theme 1

Thermo & Molecular modelling
Prof. E. Müller and Prof. G. Jackson

Fundamental transport phenomena
Prof. O.K. Matar

Industrial scale modelling
Prof. S. Macchietto
OBJECTIVES

• Research:
  – To produce a fully predictive model for fouling in refinery heat exchangers

• Technology transfer:
  – To utilise predictive models to improve monitoring, desing and operations of refinery pre-heat trains

Image courtesy of Hexxcell ltd.
Thermo & Molecular modelling

- Experimental (bulk phase) data
- Analytical Equation of state
- Parameters for the intermolecular potential
- Molecular simulation

Properties of bulk fluids

Interfacial & transport properties; mesophases
Equation of State

- Statistical Associating Fluid Theory (SAFT)
- Monomeric segments (repulsion/attraction)
- Non-spherical molecules (chains)
- Association (hydrogen bonding, chem. equil.)

**New segment-segment Mie potential**

\[
U^{\text{Mie}}(r) = C(\lambda_r, \lambda_a) \epsilon \left\{ \left( \frac{\sigma}{r} \right)^{\lambda_r} - \left( \frac{\sigma}{r} \right)^{\lambda_a} \right\}
\]

\[
C(\lambda_a, \lambda_b) = \frac{\lambda_r}{\lambda_r - \lambda_a} \left( \frac{\lambda_r}{\lambda_a} \right)^{\frac{\lambda_a}{\lambda_r - \lambda_a}}
\]

Example: VLE Predictions in Mixtures

Molecular modelling

Asphaltene aggregation using force fields derived from SAFT

n-heptane

toluene

Fundamental transport modelling

- Fluid, interfacial & transport properties
- Chemical reaction and equilibrium
- Momentum balance
- Heat balance
- Fouling deposition & removal rate
- Shear stress and pressure drops
- Heat transfer coefficient
Laminar flow - DNS

Re = 500; 2D Modelling

VOLUME FRACTION

TEMPERATURE

Viscosity

Video credits: Prof. O.K. Matar
Turbulent flow - LES

Re = 34 000; 3D Modelling

Volume Fraction

Temperature

Viscosity

Video credits: Dr. J. Yang and Prof. O.K. Matar
Impact of Surface T on Fouling Formation

Fouling formation rate increases with surface temperature

Credits: Dr. J. Yang and Prof. O.K. Matar
Industrial scale modelling

- Fluid, interfacial & transport properties
- Deposition & removal rates
- Shell-side coupled to multi-pass tube-side model
- Design, retrofit
- Costing and impact model
- Operations
Industrial scale models

\[ Q = \frac{1}{U} = \frac{1}{U_c} + R_f \]

Higher \( T \), Lower \( \nu \)

Bad performance

It fouls!

It fouls more!

The “self-fulfilling prophecy”

Courtesy of Hexxcell Ltd
High fidelity thermo-hydraulic model

Validated: Exxon, Shell (Hexxcell Ltd)

Main features:
- Multi-scale (single tube to network)
- Dynamic and distributed (geometry + local $T$, $v$, $h$, phys props ...)
- Fouling function of local conditions (EP + other models)
- Interacting thermal/fouling/fluid-dynamics (growing deposit layer)
- Thermal ageing model
- Exchanger geometry, configuration

Applications

Operations

Enhanced fouling monitoring

Control (bypass, flow split, ...)

Assessment of fouling costs

Design /retrofit

Fouling analysis

Impact on energy/CO2

Single HEX design/retrofit

HEN structure design / retrofit
Crude oil fouling - Experimental

UNIHEAT Themes 2&7

Fouling rigs
Pilot plant scale – Prof. G. F. Hewitt
Lab scale – Dr. Marcos Millan

Chemical structure and molecular weight characterization
Dr. Marcos Millan

Chemical Imaging
Prof. S. Kazarian

X-ray scattering
Prof. O. N. Martyanov

Size Exclusion Chromatography

Increasing molecular size

Retention time (min.)

Signal (Norm.)

Crude B Fresh Crude Oil
Heated Crude 200
Heated Crude 280
Heated Crude 390

X-ray scattering

Chemical Imaging

Storage

Desalter

Flash

Furnace
High Pressure Oil Rig (HiPOR)

Fouling deposits at controlled, industrial conditions

Credits: Prof. G.F. Hewitt

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Chemical Characterisation

Changes in the oil preceding/accompanying formation of deposits on surfaces or catalysts can be tracked as a function of operating conditions (temperature, pressure, crude oil blend, etc.)

Size Exclusion Chromatography

Synchronous UV-F Spectroscopy

Credits: Dr. Millan-Agorio
Small angle X-ray scattering

$$I(h) = \frac{4\pi\sin\theta}{\lambda}, \quad 2\theta \text{ range } 0.1 - 6^\circ$$

Additives for asphaltene solutions in toluene

Asphaltene aggregate

Aspect ratio 1:5:15

Asphaltene aggregation depends on solvent and additive type

Credits: Prof. O.N. Martyanov and Dr. Y.V. Larichev
Analysis of key features of the Deposits by a combination of multiple techniques

Scanning Electron Microscopy of a catalyst surface showing regions of preferential formation of carbon deposits.

Thermogravimetric analysis to determine the deposit degree of graphitisation

EDX analysis of the insoluble fraction of industrial heat exchanger deposits to determine the likely origins of deposit formation

Analysis of the soluble fraction of industrial heat exchanger deposits

Credits: Dr. Millan-Agorio
Chemical imaging with IR spectroscopy

Imaging techniques based on ATR-FTIR: non-destructive; combine chemical and spatial information; small amounts of sample required.

Credits: Prof. S. Kazarian
ATR imaging of crude deposits

Asphaltenes, carbonates, sulphates, sulfoxides, oxalates and possibly coke in refinery deposits

Energy & Fuels 2009, 23, 4059

Credits: Prof. S. Kazarian
UNIHEAT Project - Research programme

- Crude oil fouling
- Other UNIHEAT research themes
Thermodynamic power generation cycles

Thermohydraulic Generator-ORC (THG-ORCs)

Conversion of waste heat to useful power

Expander selection

Selection of liquid mixtures

Credits: Dr. CN. Markides
Liquid Stirling Engine + Catalytic Heater (LSE-CH)

- Simpler and cheaper than a Stirling engine, turbine and multiple expansion steam engine
- Low emissions
- Working fluid in liquid state can serve as lubricant for all rubbing parts
- Incompressible liquid working fluid decreases remarkably dead volume
- Catalyst heat generation: 100 – 1,000 °C
- Easily scalable: 1 W to 1 MW per cylinder
- Thermochemical heat recuperation is possible

Credits: Prof. V. Kirillov, patent pending
**Heavy oils upgrade**

**Cr-doped Al\(_2\)O\(_3\) as catalytic support**

- Al\(_2\)O\(_3\)-Cr allows NiO & MoO\(_3\) to reduce at lower temperatures
- Different distribution of coke on catalyst
- NiMo/Al\(_2\)O\(_3\)-Cr achieves better asphaltene upgrading

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction T</th>
<th>g coke/g catalyst</th>
<th>Conversion fraction&gt;450°C</th>
<th>Conversion Asphaltenes</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiMo/Al(_2)O(_3)</td>
<td>425°C</td>
<td>0.31</td>
<td>46%</td>
<td>76%</td>
</tr>
<tr>
<td>NiMo/Al(_2)O(_3)-Cr</td>
<td>425°C</td>
<td>0.45</td>
<td>52%</td>
<td>82%</td>
</tr>
</tbody>
</table>

Credits: Dr. M. Millan
Drag reduction in oil pipelines

(a) Existing continuous electrical heating

(b) Multi-point heating system using alternative gas heaters

Credits: Prof. S. Macchietto and Prof. A. Porsin
Laser Induced Pyrolysis of Light Hydrocarbons

Credits: Prof. V.N. Snytnikov
Technology transfer is difficult!

Traditional, linear approach

Science
→ Engineering
→ Applications
→ Products/Services
→ Benefits

Structured Approach + Experience

Science
→ Engineering
→ Products, Services
→ Benefits
→ Applications
→ Science

Innovation by design
3 Steps to Innovation

• Advanced Research methods, data, software

• Lab Demonstration small/medium scale

• Industrial feasibility full scale, real
3 Steps to Innovation – with industry

UNIHEAT

- Advanced Research methods, data, software
- Lab Demonstration small/medium scale
- Industrial feasibility full scale, real

Industry partners

- Engagement focus, trust, relevance
- Data, materials proof of concept
- Plant, people performance, benefit, ... steps for use

Greater probability of Technology Transfer success
IEP events

UNIHEAT Brainstorming event

VIP breakfast – UK embassy, Moscow

UK Heat transfer conference sponsorship

UNIHEAT hosts inaugural Annual Conference
UNIHEAT Office

Address: Entrance 6, 13th floor, Office 1325, Krasnopresnenskaya Nab., 12, Moscow, 123610
Office phone: +7 495 2582169
Collaboration opportunities:

- Major Partnerships (co-sponsoring the whole project)
- Bespoke projects (tailored to specific needs)
- Feasibility & Case studies
- R&D or Consultancy

“We are pleased to be involved with this very important research programme. Improving heat exchange technology remains important for the environmental efficiency of the oil processing industry. We are very pleased to team up with Skolkovo to fund Boreskov and Imperial, two of the world’s leading research institutes in this key research programme”

Scott Sloan, President of BP Russia, December 2013
What can we offer?

Advanced oil characterization techniques

Catalytic technology expertise

Energy efficiency analysis

Fouling deposit characterization

Advanced thermodynamics modelling

Catalytic heating technology

Modelling of Fundamental transport phenomena

Test runs on oil rig facilities
Acknowledgments
Contacts

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**Industry engagement:**
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