Low-grade fuel utilization: In transit to a cleaner and low carbon energy future

By Saumitra Saxena

Acknowledgments: Prof. William L. Roberts, Director, CCRC

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Energy over the Millennia: History & Mostaqbal

Can we sustain the population and economic activity for centuries & millennia to come?

The Future of Fuel: Centuryscape

Natural Gas (Methane) will be the mainstay of long-term primary energy and hydrogen economy

Age of Decarburization of Energy. Serendipity!


Decline of high carbon coal & liquid fossil fuels
Age of Decarburization of Energy-choice of right technology for Power generation

Natural Gas fired Combined Cycle Power Plants are winners
Phasing out of Coal and Oil with Natural Gas is ongoing at a rapid rate; But is it sufficiently fast to meet Global CO\textsubscript{2} emission targets? How Natural Gas infrastructure can be bolstered keeping energy security paramount?
Global Energy by Use in 21st Century

Solar Eclipse, Aug 21\textsuperscript{st} 2017: Impact on US Power Grid

Partial eclipse in California between 9:02 to 11:54 A.M. (62-76\% Sun blocked)

5 GW reduction in solar power in California during the eclipse

Data source: California ISO (http://www.caiso.com/market/Pages/ReportsBulletins/DailyRenewablesWatch.aspx)
In Transit: Coming Decades (2050)

- Global warming & Climate change
- Natural Gas as a bridge to decarbonization and inception of H₂ economy
  - Efficiency
  - Hybridization & decentralization
- Rise of Renewables
  - Intermittency & reliability
  - Storage & flexibility & fungibility
- Sector-wise fuel/technology flexibility
  - Energy Continuity & Security
  - Marine Transport (HFO, IMO 2020)
  - Aviation (Kerosene/Bio-FT); Ground (Hybrid-electric)
  - Gas turbine back-up fuels (Crude/HFO)

Role of regulatory policies and technological disruptions will be vital in charting the course
The Case for Low Grade fuels

Future energy mix will be dynamic, flexible, hybrid, distributed and driven by localized factors

No single winning combination ➔ Some role for all strategies, including low-grade fuel utilization

Devil’s advocate
What are Low Grade fuels

- Significantly lower energetic content than conventional fossil fuels
- High concentration of pollutant precursors like:
  - Sulfur
  - Asphaltene
  - Carbon residues
  - heavy metals

Source: Addressing Gas Turbine Fuel Flexibility GER4601
Majority of global reserves are light and medium sour
Most quoted benchmark prices are light sweet crude oils
• WTI (West Texas Intermediate), Western Hemisphere;
• Brent (North Sea Crude), Europe

Source: DOE, Oil & Gas Journal, Company Information (2007)
The Curious Case of Low Grade fuels

Energy losses from the well-head to the petroleum ready for customer use;
EROI is Energy Return on Investment

Less processed/ locally available fuels offer Carbon footprint reduction
Saudi Arabian Crude Oils and derived Heavy Oils

HFO: high viscosity, high molecular weight, tar-like dirty nature and high asphaltene (n-heptane insolubles) content that makes it difficult to burn.

Trace heavy metals like vanadium, nickel, lead, etc. pose additional problems like high temperature corrosion and fouling.

High sulfur contents by up to 4.5 mass % that leads to SO₂ emissions.
KAUST High Pressure Corrosion Rig

Enabling crude oil burn in **F/H-class gas turbines**: Testing of gas turbine structural materials for **hot corrosion** resistance

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Saudi Arabia power generation fuel-mix

Saudi Electricity Company (SEC) Facts for 2017

Power Capacity (56.3 GW)
- 43 Power Plants
- Steam Units (40%)
- Gas Units (38%)
- Combined Cycle (23%)

Generation Units (636)
- 44 Steam Units
- 422 Gas Units
- 131 Combined Cycle
- 28 Diesel Units
- 11 Mobile Gas Turbines

Fuel Types
- Natural Gas (39.1%)
- Crude Oil (28.1%)
- Heavy Fuel Oil (26.3%)
- Diesel Oil (6.4%)

Emissions
- Nox (408 mg/m^3)
- Sox (393 mg/m^3)
- Lower than allowed limit

Source: Middle East Economic Survey (MEES, 2013); Saudi Electricity Company (SEC, 2017)

Prices of HFO, distillate, and crude oil from Ship & Bunker historical fuel prices (historical)

Cheap, abundant, handy, flexible, local ➔ Energy security & revenue
Difficult, Inefficient, Polluting ➔ Turn the clock back

Courtesy, Jeffery Goldmeer, GE Power, FFW, KAUST, 2016
Efficiency of Industrial Gas Turbines

Combined Cycle Efficiency, %

- E-class (90-201 MW)
- F-class (200-325 MW)
- H-class (300-557 MW)
- J-class (≥550 MW)

Turbine Inlet Temperature (TIT), °C

- 1000
- 1100
- 1200
- 1300
- 1400
- 1500
- 1600
- 1700

Vintage Tech./Aero (<100 MW)

Primary Source: GE Power Systems Product Catalog (2018)
Maintenance Factor-An indicator of downtime & monetary loss

- Fuel-type
- Radiation from Soot in Combustor
- Corrosion-Na, K, V-accelerated damage to Nozzles/Buckets
- Deposits-Direct fuel contaminants or Indirect via Inhibitors for Corrosion control
- Firing Temp
- Wet/Dry NOx Control
- Start-up/Shut-down frequency
Materials: Limiting technology for Gas Turbines

Required component lives and material temperatures
(Source: Materials at High Temp. (1994), 12 (1))

Cooling, Superalloys, & Thermal Barrier Coatings (TBC) enable required material life and functionality: Source NETL
Firing Temperature and Material Capability

**Mechanical forces**
- creep
- fatigue
- erosion

**High temperature environment**
- oxidation
- hot corrosion

Beyond 2020; Towards 1700 °C TIT
- Refractory super alloys (1800 °C)-Mo/Nb/Pt/Ir based? TiAl?
- Ceramic Matrix Complex(CMC) (1500 °C)
- Sintered metal foams for Transpiration Cooling

**Current State of Art (2010-20)**

**Mitsubishi-M501 J class (1600 °C TIT):**
- Transition piece(TP) Ext. steam cooling
- High-η film cooling of blade
- Advanced TBC
- Ni-based DS alloy (MGA1400/2400)

**GE-H class (1600 °C TIT):**
- All air-cooled
- Single crystal (Ni-Fe)

**Siemens HL (1600 °C TIT):**
- Air-cooled class-Ni-DS alloy, advanced TBC
Condensation of molten salts (Sulfates & Vanadates)

Combustion gases coming in contact with turbine parts at temp below dew-point of the gas

**Formation of Sodium sulfate**

\[ 2NaCl + SO_3 + 1/2O_2 \rightarrow Na_2SO_4 + Cl_2 \]
\[ 2NaCl + SO_3 + H_2O \rightarrow Na_2SO_4 + HCl \]
\[ 2NaCl + SO_2 + O_2 \rightarrow Na_2SO_4 + Cl_2 \]

**Formation of Vanadates**

\[ V_2O_5 + Na_2SO_4 \rightarrow 2NaVO_3 + SO_3; \] Meta-vanadate; M.P.=630 °C;  
\[ V_2O_5 + 2Na_2SO_4 \rightarrow 1/2Na_3V_2O_7 + 2SO_3; \] Pyro-vanadate; M.P.=635 °C;  
\[ V_2O_5 + 3Na_2SO_4 \rightarrow 2Na_3VO_3 + 3SO_3; \] Ortho-vanadate; M.P.=850 °C;

**Condensation of molten salts (Sulfates & Vanadates)**

Combustion gases coming in contact with turbine parts at temp below dew-point of the gas
\[ Na_2SO_4 (g) \rightarrow Na_2SO_4 (l) \]
\[ V_2O_5 (g) \rightarrow V_2O_5 (l) \]
Vanadates (g) \rightarrow Vanadates (l)

**Destruction of protective oxide layer**

\[ Al_2O_3 + V_2O_5 \rightarrow 2AlVO_4; \] Cr_2O_3 + V_2O_5 \rightarrow 2CrVO_4  
(similarly NiO, CoO are formed)

**Severity of attack (Oxidation/Hot Corrosion rate)**

- **Low-temperature (type II) Hot Corrosion**
  - Sulfur dependent, below melting point of salts

- **High-temperature (type I) Hot Corrosion**
  - Sulfur independent, with molten salt

**Increasing Temperature**

- 595 °C (1100 °F)
- 705 °C (1300 °F)
- 815 °C (1500 °F)
- 870 °C (1700 °F)
- 1037 °C (1900 °F)
General Electric (GE) and KAUST teamed up to build the Corrosion Rig (2015-18)
Sample section and coupons

New material coupons

Status of coupons after hot corrosion run
Corrosion rig- fully stable and repeatable operation with Arabian Extra Light Crude Oil (AXL)

Maintaining Hot Corrosion Conditions for long durations of 500+ hours (21 days) continuously; Test protocol is for 2000 hours
Ammonia Combustion in Gas Turbines

Acknowledgments:
Dr. Mourad Younes (Saudi Aramco)
**Objective:** Demonstrate the feasibility of burning hydrogen carriers, such as ammonia, in a micro gas turbine.

**Target:** Pure ammonia operation in industrial micro gas turbine (e.g. Ansaldo T100). 2020 - 2021
Heavy Fuel Oil: Desulfurization & Combustion

Enabling availability of low-sulfur HFO in view of IMO2020: Oxidative desulfurization of Heavy Fuel Oil

Improving HFO combustion for Boilers and Marine engines: Emulsions & Additives

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Pei Xinyan, Ph. D. Post-doc fellow, Combustion
Abdul Gani, M.S. Ph. D. student Fuel characterization & combustion
Chaoqin Chen, M.S. Analytical Scientist
Abdulrahman Alkhateeb, Ph. D. student Experimental Combustion
Ayman Elbaz, Ph.D., Laser Diagnostics, Combustion
Saumitra Saxena, Ph. D. Combustion & Corrosion
William Roberts, Ph.D. Principal Investigator
Heavy Fuel (Bunker) Oil for International Marine Transport

MARPOL Annex VI sulfur limits proposed by International Maritime Organization (IMO)

<table>
<thead>
<tr>
<th>Date</th>
<th>Sulfur Limit in Fuel (% m/m)</th>
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<tbody>
<tr>
<td></td>
<td>SOx ECA</td>
</tr>
<tr>
<td>2000</td>
<td>1.5%</td>
</tr>
<tr>
<td>2010.07</td>
<td>1.0%</td>
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<tr>
<td>2012</td>
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<tr>
<td>2015</td>
<td>0.5%</td>
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<tr>
<td>2020</td>
<td></td>
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</tbody>
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International marine shipping fuel consumption (Reference case)

- High-sulfur fuel oil
- Low-sulfur fuel oil
- Distillate fuel oil
- Liquefied natural gas


HFO usage will continue to power marine industry;
HFO desulfurization most cost-effective path
Low-cost Desulfurization of HFO

Hydro-desulfurization (HDS)

Oxidative-desulfurization (ODS)

Temperature, °C

Pressure, bar

ODS – Proven technology for Ultra-Low Sulfur Diesel at Lab-scale
Lower operating cost, cheaper product fuel
Reactivity of organosulfur compounds in HDS and ODS

ODS is potentially more suitable for HFO desulfurization than HDS
Oxidative desulfurization of HFO

- **Aromaticity**
- **Size, Boiling point**

4,6 Dimethyl-Dibenoziophiophene

Dibenoziophiophene

Dibenzothiosulfone

**Refractory S-Compounds (likely)**

<table>
<thead>
<tr>
<th>Compound</th>
<th>DBE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzoziophiophene</td>
<td>6</td>
</tr>
<tr>
<td>Dibenzothiophiophene</td>
<td>9</td>
</tr>
<tr>
<td>Aromatic/Naphthenic derivatives</td>
<td>7-15</td>
</tr>
</tbody>
</table>

**Acetone extraction**

**Fourier Transform-Ion Cyclotron Resonance (FT-ICR) Mass Spectrometry**

Distribution of Hydrocarbons in HFO sample
First cut results of ODS applied on HFO

HFO desulfurized via ODS

O/S ratio: Molar ratio of Oxygen ($\text{H}_2\text{O}_2$) and Sulfur (in HFO)

Nuclear magnetic resonance (1H) spectroscopy
HFO emulsion imaging

Cryo-Scanning Electron Microscopy (SEM)

Cryo-Transmission Electron Microscopy (TEM)
Water-in-HFO Cryo-SEM imaging

Hollow-sublimated water droplet with oil remnants

Water-in-HFO, 20%, Sonication mixing no surfactant.

Solid-unsublimated water droplet

Hollow: Asphaltenes covering the skeleton of sublimated water droplet
Imaging Emulsions: Cryo-Electron Microscopy

Triple emulsion: 20% water in HFO (Sonicated); 20% in water (Mechanical)

Water-in-HFO, 20%, Sonication, no surfactant


10's nm  10's µm
HFO combustion with Magnesium based additives

10kW Swirling flame experimental set up

SEM-HFO (no additive) PM

TEM-HFO with additives PM

Flue gas pH

Breaking the Asphaltene?

10μm

Filters for PM collection

SEM-HFO with additives PM

Cold end Corrosion

S+O₂ → SO₂

SO₂+O₂ ↔ SO₃

H₂O+SO₂ ↔ H₂SO₃

H₂O+SO₃ ↔ H₂SO₄
Evolutionary (Genetic Algorithm) framework for Crude/Heavy Oil Surrogate Development

- Define n pseudo-components from the distillation curve breakdown
- Derive the critical properties of the pseudo-components
- Design n molecules to match the properties of the PCs (Physical fit).
- Choose the amount of the designed real molecules to match the chemical properties of the fuel (Kinetic fit)
- Multi-objective Optimization using Non-dominated Sorting Genetic Algorithm (NSGA)
Optimized surrogates for Diesel and HFO
New Initiative: Thermoacoustics based Waste Heat Recovery: 2018

How to valorize flue or exhaust gases that are currently rejected in the environment at high temperature (500-1200 K)?

Year 1
Prototype 600 W

Year 2-3
Prototype 20 kW

Looking for partners

TA Refrigerator prototype, PSU

TA alternator diaphragm and Piezo-electric system

Techno-economic studies for gas turbine/Solar thermal-Thermoacoustics hybrid systems
Old Tjikko, the world's oldest tree, is almost 10,000 years old
A true symbol of endurance, sustainability & longevity

"Virtue itself turns vice, being misapplied,
And vice sometime by action dignified"

Act II, Scene iii, Romeo and Juliet, William Shakespeare