Sasol: an industrial perspective

UKZN
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Sasol Technology R&D, P.O. Box 1, Sasolburg, 1947, South Africa
What type of company is Sasol?

Sasol is an integrated **Fuels** and **Chemicals** Company

Fischer-Tropsch Technology
Where did it all begin?

Dr Franz Fischer
Dr Ing Hans Tropsch

Catalytic Process for the Production of Long Chain Hydrocarbon Paraffins from Carbon Monoxide and Hydrogen

22 July 1925
Perspective on Fischer-Tropsch Synthesis (FTS) in South Africa

- Initial driver to commercialize Fischer-Tropsch Synthesis (FTS) in RSA...fuel independence on crude imports...1950
- Secondary objective to convert low grade coal to petroleum products and chemical feedstock
- Today Sasol produces >160 000 barrels per day (~ 14 000 m³) of synthetic transportation fuel and chemicals from the FTS (from 120 000 tons of coal/day)
- Sasol manufactures more than 200 different fuel and chemical products from a combination of SasolLurgi coal gasification and iron and cobalt based FTS, directly employ 26000 people, and is the biggest tax payer in RSA.
- The Fischer-Tropsch synthesis supplies in excess of 40% of RSA's liquid fuels requirements (Sasol + PetroSA),
Types of FT technology

Can be divided into three types:

- CTL – Coal to Liquids
- GTL – Gas to Liquids

BTL – Biomass to Liquids – idealised concept, not yet commercialised

Sasol
South Africa – FT plants and refineries
FT Technology: GTL & CTL Commercial Plants in the World

- **Qatar GTL**
  - Qatar Petroleum/Sasol 34,000 bpd
  - Qatar Petroleum/Shell 140,000 bpd

- **Nigeria**
  - Sasol Chevron 34,000 bpd

- **South Africa GTL**
  - Sasol 15,600 bpd
  - PetroSA 47,000 bpd

- **Malaysia GTL**
  - Shell 12,500 bpd

- **South Africa CTL**
  - Sasol 160,000 bpd

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Fischer-Tropsch technology - overview

Coal or Biomass → Gasification → Synthesis gas → HTFT - High Temperature Fischer-Tropsch → Product upgrading → LPG Gasoline Kerosene Diesel Chemicals

Natural gas → Reforming → Synthesis gas → LTFT - Low Temperature Fischer-Tropsch → Product upgrading → Olefins (to plastics)

Current LPG Naphtha Diesel
Future Kerosene Base oils

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Sasol’s integrated business model

Exploiting the benefits of Fischer-Tropsch technology

Coal, crude oil and natural gas sold to open market

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**CTL & GTL to fuels and chemicals**

**Raw materials:**
- Coal
- Crude Oil
- Natural gas

**Syngas Generation:**
- Reforming
- HT Gasification
- LT Gasification

**Fischer Tropsch:**
- LT-FT (Co)
- LT-FT (Fe)
- HT-FT (Fe)

**Upstream Leveraging:**
- Ethane cracker
- LPG
- Condensates
- LNG

**Reaction water**

**DERIVATIVES**
- Alcohols
- Ketones
- Acids
- Waxes
- Olefins/Aromatics
- Oxygenates
- Lab’s
- Monomers
- Polymers
- Co-Monomers
- Lab’s
- Det Alcohols
- Alcohols
- Solvent Blends

**Water & Environmental**

**Integrated FT Complexes**
How do we process the raw materials?

Raw materials:
- Coal
- Crude Oil
- Natural gas

Processes:
- Reforming
- HT Gasification
- Fischer Tropsch: LT-FT (Co), HT-FT (Fe)

Products:
- Carboxtar
- Phenolics & Cresylics
- Ammonia, nitric acid, fertilisers, explosives
- Methanol/DME
- Chemicals
- Olefins, Paraffins, Waxes
- Olefins/Oxygenates
- Polymers
- Alcohol, Ketones, Acids
- Gasoline, LPG, Jet Fuel, Fuel Oil
- Alcohol, Monomers, Aromatics, Base Oils, Naphtha, Solvent Blends
- Water & Environmental

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What is coal and Natural Gas?

Coal
- **Coal** is a readily combustible black or brownish-black sedimentary rock normally occurring in rock strata in layers or veins called **coal beds**
- Coal is composed primarily of carbon along with variable quantities of other elements, chiefly sulphur, hydrogen, oxygen and nitrogen
- Various types of coal – peat, lignite, sub-bituminous coal, bituminous coal, anthracite and graphite
- Obtained by mining – underground or open pits (open cast mining)

Environmental issues
- Release of carbon dioxide - a greenhouse gas
- Waste products – ash and heavy metals
- Acid rain from high sulphur coal
- Interference with ground water
- Impact on human health
Structure of coal

A Representative Macromolecular Structure of a Bituminous Coal [Levine et al, 1982; Wiser, 1978]
**Natural Gas**

- **Natural gas** is a gas consisting primarily of methane.
- Also contains other hydrocarbons – ethane, propane, butane and pentanes.
- It is found associated with other fossil fuels, in coal beds, as methane clathrates, and is created by methanogenic organisms in marshes, bogs, and landfills.
- It is an important fuel source, a major feedstock for fertilizers, and a potent greenhouse gas.

**Environmental**

- *Produces about half the amount of CO₂ compared to coal*
- *Sulphur compounds and NOx – less than coal*
Distribution of natural gas – by countries in cubic metres per year
How do we generate syngas?

Syngas generation:
- Gasification
- Reforming
Gasification

Gasification is a process that converts carbonaceous materials, such as coal, or biomass, into carbon monoxide and hydrogen by reacting the raw material at high temperatures with a controlled amount of oxygen and/or steam.

The resulting gas mixture is called synthesis gas or syngas.
Processes during gasification

- The pyrolysis (or devolatilization) process occurs as the carbonaceous particle heats up. Volatiles are released and char is produced, resulting in up to 70% weight loss for coal.

- The combustion process occurs as the volatile products and some of the char reacts with oxygen to form carbon dioxide and carbon monoxide, which provides heat for the subsequent gasification reactions

\[
\begin{align*}
    C + \frac{1}{2} O_2 & \rightarrow CO \\
    C + O_2 & \rightarrow CO_2
\end{align*}
\]

- The gasification process occurs as the char reacts with steam to produce carbon monoxide and hydrogen, via the reaction

\[
C + H_2O \rightarrow CO + H_2
\]
Four types of gasifier are currently available for commercial use: counter-current fixed bed, co-current fixed bed, fluidized bed and entrained flow.
Gasification – value chain

- Primary product – syngas

- Other products or co-products
  - Tars and pitch
  - Ammonia
  - Phenolics – xylenols, cresols and phenols
  - Sulphur
Natural Gas Reforming

\[ \text{CH}_2' + \text{H}_2\text{O} \rightarrow \text{CO} + 2\text{H}_2 \]

\[ \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \]
How do we process syngas in FTS?

Fischer Tropsch:
- LTFT (Co)
- LTFT (Fe)
- HTFT (Fe)
FT: composite of two reaction mechanisms

- CO hydrogenation reaction

  \[ \text{CO} + 2\text{H}_2 \rightarrow \text{C}_1^* + \text{H}_2\text{O} \text{ (Exothermic)} \]

- Polymerisation reaction

  \[ \text{C}_1\text{-C}_1\text{-C}_1\text{-C}_1^* + \text{C}_1^* \rightarrow \text{C}_1\text{-C}_1\text{-C}_1\text{-C}_1\text{-C}_1\text{-C}_1^* \]

  \[ \text{C}_n^* + \text{C}_1^* \rightarrow \text{C}_{n+1}^* \]
**Fischer-Tropsch reaction schematic**

Conversion of synthesis gas to hydrocarbons

\[ \text{CO} + 2\text{H}_2 = -(\text{CH}_x) - + \text{H}_2\text{O} \]  
(exothermic)

Step-wise *polymerisation* process
Sasol’s classification of FT Technology

- **Iron-based High-temperature FT (Fe-HTFT)**
  - Secunda
  - 350°C: “Lighter” product spectrum
  - Two-phase system: gas-solid

- **Iron-based Low-temperature FT (Fe-LTFT)**
  - Sasolburg
  - 240°C: Heavy product spectrum (waxes)
  - Three-phase: gas-liquid-solid

- **Cobalt-based Low-temperature FT (Co-LTFT)**
  - Qatar
  - 230°C: Heavy product spectrum (waxes)
  - Three-phase: gas-liquid-solid
FT primary reaction products

- Low temperature FT reaction
  - Mainly normal paraffins (saturated, straight chain hydrocarbons, wax)
  - Carbon number distribution determined by reaction conditions, reactor type, reactant partial pressures, and catalyst
  - Small amounts of olefins, alcohols and acids
  - Most suitable for diesel fuel and synthetics lubricant production

- High temperature FT reaction
  - Mainly olefinic and aromatic hydrocarbons
  - Very little heavier products, high C1-C3 gas yield
  - Large amounts of oxygenated products
  - Most suitable for gasoline and chemical production
Comparison of carbon number distribution

![Graph showing carbon number distribution for HTFT (iron fluidised bed, 340°C), LTFT (cobalt slurry phase, 220°C), and LTFT (iron slurry phase, 240°C).]
Fe-FT Technology

- Two types of FT processes
  - High Temperature Fischer-Tropsch (HT FeFT)
  - Low Temperature Fischer-Tropsch (LT FeFT)

- HT FeFT
  - Produces lighter components (C1 to C20)
  - Produces oxygenates in highest quantities
  - Basis for petrol and chemicals
  - Fluidised bed reactor

- LT FeFT
  - Produces heavier components (>C20)
  - Produces oxygenates in lower quantities, wax is major product
  - Basis for wax and paraffins
  - Slurry Reactor
**Effect of temperature on Iron-based FTS**

*Product distribution (per 100 carbon atoms)*

<table>
<thead>
<tr>
<th>Product</th>
<th>Low Temperature 220 - 250°C</th>
<th>High Temperature 330 – 350°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alpha ~ 0.95</td>
<td>Alpha ~ 0.7</td>
<td></td>
</tr>
<tr>
<td>CH$_4$</td>
<td>4</td>
<td>7</td>
</tr>
<tr>
<td>C$_{2-4}$ olefins</td>
<td>4</td>
<td>24</td>
</tr>
<tr>
<td>C$_{2-4}$ paraffins</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>Gasoline</td>
<td>18</td>
<td>36</td>
</tr>
<tr>
<td>Distillate</td>
<td>19</td>
<td>12</td>
</tr>
<tr>
<td>Oils and waxes</td>
<td>48</td>
<td>9</td>
</tr>
<tr>
<td>Oxygenates</td>
<td>3</td>
<td>6</td>
</tr>
</tbody>
</table>
HT-FeFT

- Reactors – CFB and SAS
- Operation of SAS
- Products formed
HTFT – Circulating Fluidised Bed (CFB) Reactor
HTFT – Sasol Advanced Synthol (SAS) Reactor

- Gas product out
- Cyclones
- Catalyst Bed
- Cooling coils
- Gas in
Operation of SAS

- 10m reactors (diameter)
- Gas enters from the bottom – not pure syngas
- Syngas and carbon dioxide – WGS reaction
  \[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \]
- Gas interacts with solid catalyst
- Upward flow of gas causes fluidisation of bed
- Improves feed/catalyst interactions
- Gas products formed – exit through top of reactor
- Cyclones in reactor trap and recycle catalyst particles
Reactions in HTFT

\[ nCO + (2n + 1)H_2 \rightarrow C_nH_{2(n+1)} + nH_2O \]  
(for paraffins)

\[ nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O \]  
(for olefins)

\[ nCO + (2n - 1)H_2 \rightarrow C_nH_{2n}O + (n - 1)H_2O \]  
(for carbonyls)

\[ nCO + 2nH_2 \rightarrow C_nH_{2(n+1)}O + (n - 1)H_2O \]  
(for alcohols)

\[ nCO + (2n - 2)H_2 \rightarrow C_nH_{2n}O_2 + (n - 2)H_2O \]  
(for acids)
**Fe – LTFT : Slurry phase**

- 200-240°C
- Precipitated Iron-based catalyst
- 5m diameter
- 100 kt pa (2500 bbl/d)
- More isothermal
- Lower dP across catalyst bed
- Online catalyst replacement possible
- Products – mainly wax and paraffins
Selectivity of FT-processes

- **CH4**
- **C2-C4 Olef**
- **C2-C4 Paraf**
- **Gasoline**
- **Mid Dist**
- **Wax**
- **Oxyg**

**Graph Labels:**
- **LTFT**
- **HTFT**
CTL & GTL to fuels and chemicals

Raw materials:
- Coal
- Crude Oil
- Natural gas

Syngas Generation:
- Reforming
- HT Gasification
- LT Gasification

Fischer Tropsch:
- LT-FT (Co)
- LT-FT (Fe)
- HT-FT (Fe)

Power, Water, CO₂ Utilisation
- Reduction Gas; Hydrogen

Transport Fuels, Fuel Cells

Methanol/DME

SynGas To Chemicals

LPG
- Gasoline
- Diesel
- Jet Fuel
- Fuel Oil

Base Oils
- Naphtha

Refining & Fuels

Oil

LPG

Reforming

HT Gasification

LT Gasification

Fischer Tropsch:
- LT-FT (Co)
- LT-FT (Fe)
- HT-FT (Fe)

Paraffins

Fuels

Gasoline
- Diesel
- Jet Fuel
- Fuel Oil

Refining

Naphtha

Gasoline

Jet Fuel

Fuels

Paraffins

Alcohols

Ketones

Aromatics

Olefins

Olefins

Alcohols

Nitrates

Nitrogen

Ammonia, nitric acid, fertilisers, explosives

Carbotar

Phenolics

Cresyls

Water & Environmental

Methanol/DME

Syngas To Chemicals

Wax

Oxidation

BLEND

OLFINS

AROMATICS

OLFINS

AROMATICS

Xylene

Toluene

Benzene

DERIVATIVES

Water & Environmental

Integrated FT Complexes

DERIVATIVES

Upstream Leveraging
- Ethane cracker
- LPG
- Condensates
- LNG

Raw materials:
- Coal
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Syngas Generation:
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Transport Fuels, Fuel Cells

Methanol/DME

Syngas To Chemicals

LPG
- Gasoline
- Diesel
- Jet Fuel
- Fuel Oil

Base Oils
- Naphtha

Refining & Fuels

Oil
Solvents - Chemical Recovery

reaction water

Primary separation

Carbonyl recovery

- acetone
- MEK
- methanol

aldehydes

alcohols

- 95% ethanol*
- HPE

- i-propylol
- EA

- n-propylol*
- NPA

- i-butylol
- sabutol

Acid recovery

- acetic acid
- propionic acid

Alcohol recovery

- 99.9% ethanol
- n-propanol

* Also sold as final products
## Ethanol and Ethyl acetate

- **Ethanol** – acetaldehyde hydrogenation
  - *Ni catalyst*
  - Excellent selectivity – 99%
  - Side reactions – impact on product quality

- **Ethyl acetate** – ethanol dehydrogenation
  - *Cu catalyst*

(A) $\text{HOCH}_2\text{CH}_3$ (ethanol)

(B) $\text{CH}_2\text{=CHOH}$ (acetaldehyde)

(C) $\text{HOCH}_2\text{CH}_3$ (ethanol)

(D) $\text{COCH}_2\text{CH}_3$ (ethyl acetate)
## FTFT Product distribution – (oxygenates) Fe

<table>
<thead>
<tr>
<th></th>
<th>Iron slurry bed</th>
<th>Iron fluidised bed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(240°C)</td>
<td>(340°C)</td>
</tr>
<tr>
<td>Acetic acid</td>
<td></td>
<td>0.84</td>
</tr>
<tr>
<td>Propionic acid</td>
<td></td>
<td>0.19</td>
</tr>
<tr>
<td>Butyric acid</td>
<td></td>
<td>0.11</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>0.5</td>
<td>2</td>
</tr>
<tr>
<td>Propionaldehyde</td>
<td>0.1</td>
<td>0.5</td>
</tr>
<tr>
<td>Acetone</td>
<td>4.0</td>
<td>23</td>
</tr>
<tr>
<td>MEK</td>
<td>0.3</td>
<td>6</td>
</tr>
<tr>
<td>Methanol</td>
<td>24</td>
<td>0.5</td>
</tr>
<tr>
<td>Ethanol</td>
<td>45</td>
<td>40</td>
</tr>
<tr>
<td>n-Propanol</td>
<td>13</td>
<td>12</td>
</tr>
<tr>
<td>i-Propanol</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>N-Butanol</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>S-Butanol</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>i-Butanol</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Ref: Fischer-Tropsch Technology, Studies in Surface Science & Catalysis 152, Authors: AP Steynberg; ME
**Olefins**

- Extractive distillation
- Olefins that are extracted – hexene, octene and pentene
- Ethylene and propylene – gas product
- Octene – also synthesised via 1-heptene
  - *Hydroformylation to produce octanal*
    
    \[
    R_1\ce{C=CH_2} + \text{CO}/\text{H}_2 \xrightarrow{\text{catalyst}} R_1\ce{C(CH_3)C(=CH_2)}
    \]

  - *Hydrogenated to octanol*
    
    \[
    R_1\ce{C(CH_3)C(=CH_2)} + \text{H}_2 \xrightarrow{\text{catalyst}} R_1\ce{C(CH_3)C(CH_3)CH_2\text{CH}_2\text{OH}}
    \]

  - *Dehydrated to 1-octene*
    
    \[
    R_1\ce{C(CH_3)C(CH_3)CH_2\text{CH}_2\text{OH}} \xrightarrow{\text{catalyst}} R_1\ce{C(CH_3)C(CH_3)CH_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH} = \text{CH}_2} + \text{H}_2\text{O}
    \]
Fuels - Refining

Crude Oil Distillation: The First Step

- **Temp (°C)**
  - <30°C
  - 30-90°C
  - 90-180°C
  - 180-230°C
  - 230-350°C
  - 350-500°C
  - 500+°C

- **Product Recovered**
  - Butane & Lighter
  - Light Straight Naphtha
  - Naphtha
  - Kerosene
  - Distillate
  - Heavy Gas Oil
  - Residuum

- **Unit/Use Sent to**
  - Gas Processing
  - Gasoline Blending
  - Catalytic Reforming
  - Hydro-Treating
  - Dist. Fuel Blending
  - Fluid Catalytic Cracking
  - Coking
Some terms

- LPG = liquefied petroleum gas
- Petrol = gasoline (naphtha = raw petrol)
- Distillate = Precursor to diesel
- Kerosene = jet fuel or commercial paraffin
- Coke = carbon
Key activities in refining - Secunda

Separation
  - Mostly separating into light & heavy streams

Upgrading
  - Converting molecules into more valuable products

Fuel specs
  - Addressing product quality issues

Chemicals
  - Extracting or forming chemicals
Environmental

ENVIRONMENTAL
Areas covered in environmental control

Air Emissions
- $H_2S$
- VOC’s
- Greenhouse Gases
- Boiler Emissions

Aqueous Effluents
- Saline Waters
- Water Utilisation

Solid and Hazardous Wastes
- Sulfolin Liquid
- Benfield Carbonate Solution
- Bio Sludge
- Coal Tar Filter Sludge
- Catalyst Waste
Firstly - Current operational environmental footprint

Gaseous Emissions
- H₂S = 89 000 t/a
- VOC’s = 164 000 t/a
- SOx = 223 000 t/a
- NOx = 166 000 t/a
- PM = 8300 t/a

GHG emissions = 73.1 million t/a

Water use = 161 billion l/a

Solid Wastes
- Hazardous = 270 000 t/a
- Non-Hazardous = 1 126 000 t/a

Aqueous Effluents
- 42 billion litres/a

Data from Sasol Sustainability Report - 2007
Environmental Mitigation Projects

**Pollutant**
- Water
  - Water Re-use
    - Blowdown upgrade
    - Zero Liquid Effluent Design - ZLED
    - Dry Cooling
    - Anaerobic vs. Aerobic digestion
  - Salt/Ash Management
    - Black products remediation
    - Waste Re-use e.g. Bricks, Cement
- Solid Waste
- Air Pollutants
  - H₂S emission reduction
  - Improved Fuel quality e.g. remove metallic additives
  - Boiler Technology e.g. CFB
- GHG
  - Energy Efficiency
  - Carbon Capture and Sequestration
  - Non-fossil fuel based energy sources

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**Water - Project Highlights**

- Process Cooling Tower (CT) blow-down recovery

- Reverse Osmosis technology proposed with filtration technology
  - Efficacy of selected filtration process as pre-treatment
  - No commercial example available using typical Sasol Effluents

- Bio-treated effluent bulk of Process Cooling Tower make-up
  - CT recirculating water high in organics

- Biological treatment of organic effluent streams

- Biological treatment of combined effluent stream
  - Gasification effluent, Reaction Water, Oily sewer (API)

- Technology options being considered:
  - Membrane Bio-Reactor (MBR)
  - Moving Bed Bio-reactor (MBBR)
  - MBBR followed by Ultra filtration treatment

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Atmospheric Gaseous Emissions - Sasol

- **Greenhouse Gases**
  - $CO_2$
  - Methane
  - Nitrous Oxide ($N_2O$)

- **Air pollutants**
  - SOx, NOx, Particulate Matter (PM), Heavy metals
  - Sulphur in coal ends up as $H_2S$ or in ash from gasification

- **Carbon footprint**
  - Inherent process inefficiencies
  - Thermodynamic constraints
  - Utility generation

- Sasol actively considering different carbon mitigation options for existing and new plants
GHG Mitigation Possibilities

- Improve efficiency
  - Demand side
  - Supply side

- Sequester
  - Direct capture
  - Natural sinks

- Decarbonisation
  - Renewables
  - Nuclear
  - Lower C:H ratio

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Geological Storage Map of South Africa being developed - Mid 2010
Alternative Energy Options

- Solar
- Nuclear
- Hydro-electricity
- Biomass
- Geothermal
- Tidal
- Wind
Solid Waste Sources

- Fine Coal depending due to Secunda coal properties
- Slag from Gasification
- Ash from combustion, gasification and incinerators
- Hydrocarbon Sludge and biosludge
- Spent catalyst
- Legacy wastes e.g. asbestos

- Generated Hazardous waste - **270 kt** in 2006
- Generated Non-hazardous waste – **1126kt** in 2006
Cleaner Technology

- Conversion to natural gas (NG) from coal
  - Sasolburg conversion in 2005 (CTL to GTL)
  - Elimination of gasification sludge
  - Led to elimination of black products
  - Secunda will be generating power from NG - 280MW

- Co-firing of biomass in gasification processes
  - Introduction of renewables, reducing fossil fuel use

- Selection of gasification technology for coal based processes
  - Sasol developing its own FBDB technology

FBDB – Fixed Bed Dry Bottomed
Beneficial Reuse and Recycle

- Waste Recycling Facility
  - Instituted in Secunda and linked to a waste water treatment process to manage sludge produced

- Ash Utilisation
  - Ash Bricks; Cement manufacture
  - Geopolymers; Road sub-base; Raw feed for cement clinkers
  - Sasolburg ash used in manufacture of bricks

- Recovery of energy from wastes
  - Exploit the calorific value in wastes
  - New technologies emerging around the world for the recovery of energy and products from wastes