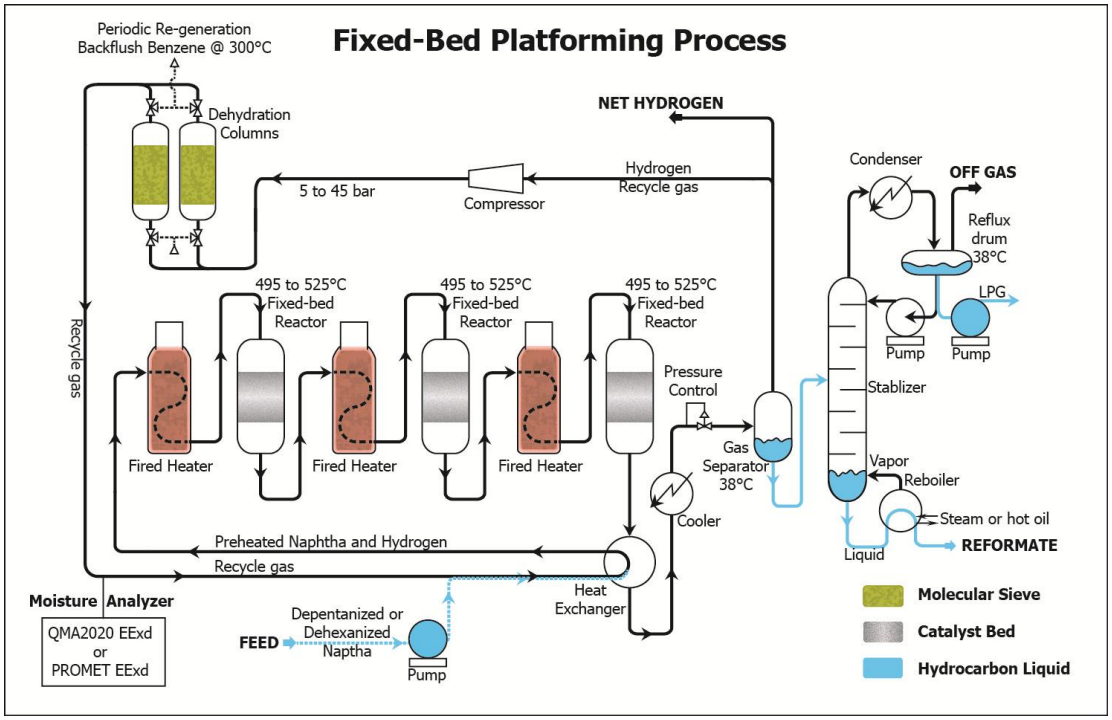
Fixed-bed Semi-regenerative Platforming process - Critical moisture measurement in hydrogen rich re-cycle gas

For fixed-bed Platforming process with radial flow reactors, maintaining low moisture concentration within the hydrogen re-cycle gas is critical to the efficient operation of this catalytic process. Increased moisture concentration results in coke formation within the 3-stage reactors using platinum and radium catalyst. Such coking reduces the operating period for the catalyst beds between regeneration cycles, with direct financial implications for refinery production efficiency.

Refinery Platforming processes a feedstock of heavy naptha, a crude oil distillate fraction with boiling point 100 to 160°C comprising mainly straight chain alkenes that are combined with hydrogen rich re-cycle gas, in a two phase liquid/vapour mixture which is heated to be wholly vaporous. This vaporous HC/H2 feedstock passes through multiple reactors, in which endothermic reactions take place. Intermediate heating is necessary to maintain the vapour phase through each of three-stage radial flow reactor beds. The product from the reactions is reformate; high octane complex hydrocarbon rings with high aromatic content. The reformate has higher energy content than the straight chain naptha feed, and forms an important part of the blending of lead-free gasoline fuels. The other product from the reactors is hydrogen, used both for re-cycle within the Platforming process and also as a net product to other processes within the refinery. The net yield of hydrogen combines into the naphta hydrotreating and isomerization processes. Typically, Platforming coverts the naptha feed into 85% liquid reformate, 10% hydrogen and 5% LPG. Lighter naptha, comprising C5 and C6 hydrocarbons, are processed separately through catalyst isomerisation, as Platforming these fractions would yield undesirable benzene and cracking into fuel gases.



Platforming reactor beds contain a platinum and radium catalyst on microporous alumina strata, offering 200 cubic metres of surface area per gram. The term 'Platforming' is a UOP trademark name derived from platinum and reforming. As the reaction stages are highly endothermic the catalyst beds are inter-linked via heaters to sustain a sufficiently high reaction temperature, about 500°C at the inlet of the reactors. For fixed-bed reactors, the operational period between catalyst regeneration cycles is 6 to 12 months dependant on the rate of coke build-up within the bed. Minimising the rate of coke formation depends on maintaining an acidic function achieved by a balance of trace chloride (0.5 to 1.0 ppmV Tetrachloroethylene) and moisture within the process fluid, for which the optimum moisture content is 15 to 25 ppmV. Higher or lower moisture concentrations, and consequent increase or reduction in acidic function, result catalyst poisoning or increased coking respectively. Increased coke build-up requires increased reactor temperature to maintain the level of catalytic activity but also further accelerates the rate of coke formation. Only strict control of moisture concentration can achieve maximum catalyst bed lifetime. Regeneration cycles require five days to complete during which the coke is burnt off in stages by the addition of increased proportions of oxygen into the catalyst bed at controlled temperature. After coke burning, the catalyst is reconditioned, called 'oxy-chlorination', by a combined treatment of air and trace HCl under high temperature. After this step the catalyst is dried with hot nitrogen and subsequently brought into active condition by reducing the surface with hot hydrogen. This process is called semi-regenerative Platforming, as each reactor bed will undergo regeneration periodically in sequence.

To maximise the interval between catalyst regeneration, operators continuously monitor moisture in the hydrogen gas re-cycle to maintain 15 to 25 ppmV within the comingled naptha/hydrogen feed within the Platforming process. To assure the correct feed condition, less than 1 ppmV moisture content is required in the H2 re-cycle, typically 0.1ppmV, processed by molecular sieve desiccant in a twin column configuration. Periodic regeneration of the bed is required, achieved by back flushing with liquid benzene at 300°C. Process plant operators activate drier bed regeneration when the actual measured moisture content reaches greater than 1 ppmV, so yielding cost and efficiency benefits over a fixed time based interval.

Molecular sieve dehydration columns

Due to reduced productivity during regeneration, UOP developed Continuous Catalyst Regeneration. In CCR units a proportion of the catalyst is extracted from the bottom of continuously operating reactors into a regeneration stack in which coke burning, oxy-chlorination and drying take place in sequential zones. After re-activation with hydrogen the catalyst is returned to the top of the reactor columns. CCR units maintain catalyst activity without shut-down for operating periods of 3 to 6 years. Maintaining trace moisture in re-cycle H2 to sub-ppmV levels is also a requirement for CCR processes. Axens IFP Octanizing is an equivalent CCR process.
Design capacities of Platformer units vary from 1000 - 4500 tons/day. Operating pressures vary from 3.5 barg up to 30 barg. CCR's operate in the lower pressure range, increasing yield of liquid reformate, as cracking reactions are reduced, but the lower partial pressure of hydrogen increases rate of coke formation, hence only CCR units operate at lower pressures.

Typical installation of Promet EExd in UOP Platforming process

Michell Solutions:

For gas phase measurements both Quartz Crystal Microbalance and Ceramic metal-oxide sensing technologies can be applied.

QMA601 or **Promet EExd/I.S.** Process Moisture Analyzer with Trace Moisture Sampling System monitoring the H2 re-cycle return into the Platforming process from the molecular sieve drier.

On semi-regenerative Platforming, the nitrogen gas used in some process configurations for drying the catalyst bed after coke burn is also an application for **QMA601** or **Promet EExd/I.S.**

For liquid phase measurements the Ceramic metal-oxide sensing technology is applied.

Light naptha liquid feed to Isomerization (UOP *PENEX* or Axens IFP equivalent) is also a key Michell application in petroleum refineries, in this case for **Liquidew EExd/I.S.**
For more information refer to published case studies:

Tamoil Refinery, Switzerland - Catalytic isomerisation plant – Axens IFP – Process Industry News – *Annual Buyers Guide 2008*

API Refinery, Italy - Catalytic isomerisation plant – UOP *PENEX. An Italian Job* - Hydrocardon Engineering – *October 2010*

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