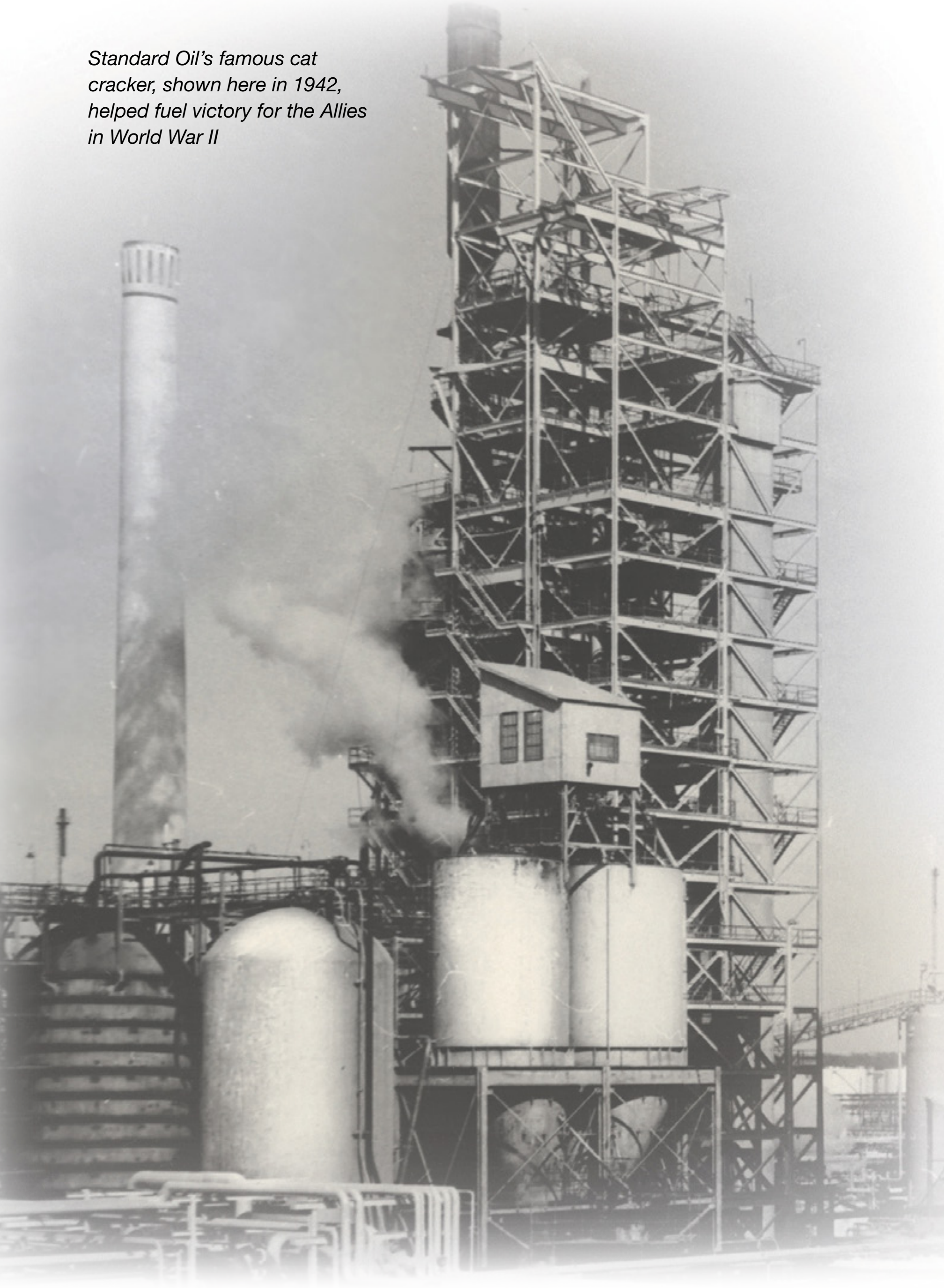
Fuelling a way of life



Standard Oil's famous cat cracker, shown here in 1942, helped fuel victory for the Allies in World War II

Fluid catalytic cracking has been called 'the most revolutionary chemical engineering achievement of the early 20th century'. **Claudia Flavell-While** finds out why

IT IS hard to imagine modern living without light hydrocarbons. We would, quite literally, be going nowhere fast without petrol or high-octane aviation fuel. Oil-based plastics such as polyethylene and polypropylene are found in everything from sandwich wrappers to textiles, not to mention heating oil and countless other polymers and chemicals produced from hydrocarbons in downstream processes.

Yet this ubiquitous feedstock of modern life in all its aspects would be a lot rarer – not to mention a great deal more expensive – if it wasn't for the workhorse of the refining industry, the fluid catalytic cracking (FCC) unit.

Some 400 FCC units are in operation around the world today. And each and every one of them can trace its ancestry back to one such unit, the Model I FCC, which started up in Baton Rouge, Louisiana, on 25 May 1942.

The 17,000 bbl/d unit was largely the brainchild of four chemical engineers, the "four horsemen", working for the New Jersey company Standard Oil. They were Donald Campbell, Homer Martin, Eger Murphree and Charles Tyson.

The development was the result of a dispute over a licensing fee. The Houdry process, which at the time was the best process for breaking heavy long-chain hydrocarbons into shorter and more useable fractions, cost too much to license so Campbell, Martin, Murphree and Tyson set out to find a way around the patents.

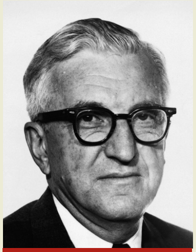
Houdry paves the way

The Houdry process was the first to make catalytic cracking commercially viable. Unlike modern crackers, Houdry's unit employed a semi-batch process with a fixed bed of catalysts. The process was developed by French mechanical engineer Eugene Houdry and pharmacist EA Prudhomme and initially used lignite coal as a feedstock, and an acid-treated clay catalyst or silica-alumina mixture catalyst.

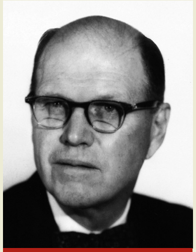
While a demonstration plant that started up in 1929 showed that Houdry's process was not commercially viable at that stage, his breakthrough was to understand why catalysts used to crack the hydrocarbon chains were very quickly deactivated by the formation of a layer of coke on the catalyst surface. The catalyst has an active lifespan measured in mere seconds before the coke layer is formed. While it's possible to remove the coke – chiefly by heating and burning it off – this process takes several minutes. So a batch plant would only be active for a very short percentage of its operating life and spend the rest of the time regenerating, making the cracking process uneconomical.

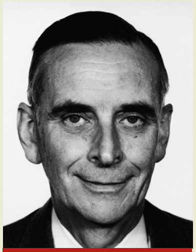
Houdry moved to the US, where, funded by the Vacuum Oil Company and later Sun Oil, he continued working on his process. Not only did he work out how the catalyst became deactivated, but he also devised the first practical way of regenerating the catalyst without shutting down

The 'four horsemen' of fluid catalytic cracking


Donald Campbell


Homer Martin


Eger Murphree


Charles Tyson

production entirely. Houdry's first solution was to build multiple reactors, so at any given time some of the reactors are in operation while the others are regenerating. The first Houdry unit was built at Sun Oil's Marcus Hook oil refinery in Pennsylvania in 1937, and more followed as the US military recognised the potential of catalytic cracking to supply large quantities of much-needed aviation fuel for the war in Europe.

The introduction of thermafor catalytic cracking (TCC) in 1941 made the process semi-continuous by placing the catalyst in a bucket on a conveyor belt linking regeneration and operating kiln. Even so, the process would eventually be outcompeted by moving bed reactors.

tiptoeing round the patent

When rival companies saw the success of Houdry's process they were keen to enter the market too but were reluctant to pay the hefty $50m licensing fee. As a result, the Catalytic Research Associates (CRA) consortium in 1938 brought together Standard Oil of New Jersey (today, Exxon Mobil), Standard Oil of Indiana (Amoco), Anglo-Iranian Oil (BP), Texas Oil (Texaco) and Dutch Shell, the engineering contractors MW Kellogg and Universal Oil Products (UOP), and Germany's IG Farben (BASF/Bayer/Hoechst).

CRA asked Campbell, Martin, Murphree and Tyson to find another way. Their aim was to find a continuous process that would maximise the contact area between the catalyst and the crude oil before moving the deactivated catalyst from the cracker to the regeneration chamber without shutting down the cracker, and without allowing the air from the regeneration chamber to come into contact with the hydrocarbons in the cracker.

> **"These were chemical reactors much larger than had ever been built for any reaction and they used a catalyst that had to be regenerated every few minutes"**

Screw conveyors could achieve this in small units but were difficult to scale up, mainly because of their tendency to clog up and because of excessive wear.

The four horsemen worked with Warren Lewis and Edwin Gilliland at MIT, who suggested that a powdered catalyst might behave like a liquid if a gas was blown through it at low velocity. While it was well known that powders could be blown up or down vessels using high-velocity gas it had not been attempted with gases at low velocities.

To get the desired 'flows-like-a-liquid' effect, operators had to use a very fine powdered catalyst such as a zeolite powder. The catalyst is mixed with vaporised oil flowing at low velocity. The vapour/solid mixture flows through the reactor like a liquid while the cracking reaction takes place. The cracked vapours are then separated from the spent catalyst with the aid of a steam stripper, and the catalyst transferred to the catalyst regenerator where the coke is burnt off before the catalyst is recycled.

This idea led to the development of the first-ever fluidised catalytic cracking unit, (US patent no 2,451,804: *A method of and apparatus for contacting solids and gases*).

"There were many problems to be solved in going to the tremendous-sized reactors needed," Gilliland wrote in a biographic note on the events. "These were chemical reactors much larger than had ever been built for any reaction and they used a catalyst that had to be regenerated every few minutes."

commercial reality

MW Kellogg, partner in the consortium, got tasked with building a 100 bbl/d pilot plant for the process, which duly started up at Standard Oil of New Jersey's Baton Rouge refinery in May 1940. The first full-scale version with an initial capacity of 13,000 bbl/d followed one year later, while the first plants of the improved Model II variant, which was more efficient and required less steel to build, were started up in 1942 and 1943. If anything bears testimony to how little the process has changed, it's the fact that both of these very first Model II units – PCLA2 and PCLA3 – operate to this day at Baton Rouge, Louisiana. Their forebear, PCLA-1, was shut down and dismantled during the 1960s.

The need to conserve strategic materials such as steel, piping and valves during wartime favoured fluid bed catalytic crackers over fixed-bed models, which were less economical with such materials. Soaring demand for high-octane aviation fuel and synthetic butyl rubber to fuel the war in Europe meant that by 1945, no less than 34 more FCC units had been built. It is estimated that FCC increased the US production of aviation fuel by 6000%, overcoming a serious shortage and handing the allies an important advantage in the war. At the same time, cat cracking yielded the butadiene needed to produce synthetic rubber, as a result of which the US was able to cut its dependence on natural rubber imports from Southeast Asia.

Gilliland later wrote: "The demand for gasoline was so great that the construction of 32 fluid catalytic cracking plants was underway before the first commercial plant was in operation, but Murphree had concluded that the process was sound on the basis of small-scale tests and was bold enough to proceed. The successful operation of these plants demonstrated the soundness of his judgment."

a lasting legacy

The thirst for light hydrocarbons did not stop at the end of World War II, thanks to rapid growth in private car ownership, chemicals demand and the rise of commercial aviation.

While there have been some incremental improvements – chiefly with regards to the catalyst – the process itself is largely unchanged from the four horsemen's innovation. The principle of fluidised bed reactors meanwhile has been adapted to many different processes across a broad range of other chemical syntheses, polymerisations, and even for the simple transport of particle products such as flour, rice and cement.

Fortune magazine, in its October-November 1951 issue, called FCC "what many engineers consider the most revolutionary chemical engineering achievement of the last 50 years." **tce**

Next month: Waldo Semon – the chemical engineer who turned PVC from a waste material into a goldmine