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Catalysis Today 29 (1996) 171–178

CATALYSIS TODAY

Efficient catalytic processes for the manufacturing of high-quality transportation fuels

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Abstract

Manufacturing of transportation fuels incorporates a number of generations of technology, viz. (1) refining processes to arrive at the desired product quality, (2) conversion processes to balance the feedstock supply with the product demand, (3) processes to steer product composition and (4) synthetic fuels. In going from (1) to (4), the thermal efficiency of the processes tends to decrease and is affected by a number of (process) principles which are discussed here. Recent progress and future needs are discussed for all four areas of fuel manufacturing.

Keywords: Transportation fuels; Fuel manufacturing

1. Introduction

With an annual world demand of 1400 million ton, transportation fuels are by far the most important products from oil. Some characteristics of the three main fuels used in the transport sector — gasoline, kerosene and diesel — are summarised in Table 1. The economic importance can be further attested to by the considerable growth in demand over the years which is expected to continue (Fig. 1).

One important characteristic of these fuels is that their state of aggregation at ambient conditions is liquid. The logistics in the transport sector these days are to a major extent geared towards the handling of liquids, thereby sustaining this preference. This preference for liquids can be further illustrated by inspection of the 'spot market' values of the main energy raw materials and products. In Fig. 2, 1992 price data for these — at a crude oil price of 20 US$/barrel — are plotted as a function of their respective atomic hydrogen-to-carbon ratio. Going from low to high H/C ratio we move from solids via liquids to gases with a clear maximum for the liquid (transportation) fuels. This plot illustrates the economic forces driving conversion of either gases (e.g., LPG via alkylation) or solids (e.g., heavy residues via cracking) to liquids.

In addition to the state of aggregation, the quality of the transportation fuels is a primary concern for the oil industry. The oil refinery owes its name to this first and most important manufacturing process. The fuel quality relates to many parameters, of which the burning characteristics are important (cf. Table 1). Many others affect driveability aspects as well but will not be discussed here.

In Table 2, four generations of energy conversion processes are presented: the first deals with product quality and hydrodesulfurisation

0920-5861/96/$32.00
SSDI 0920-5861(95)00258-8

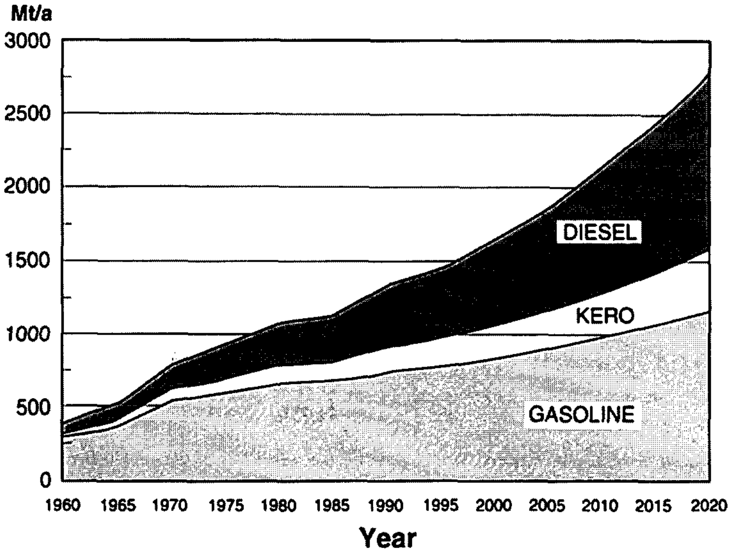

Fig. 1. Growth in global demand of world transportation fuels.

(HDS) to lower the sulfur level of products and catalytic reforming for the enhancement of the octane quality of gasoline are prime examples.

The second generation is that of conversion of heavier (e.g., residue cracking) or lighter (e.g., alkylation) oil fractions to — in these cases — gasoline. These processes are only economic at a minimum oil price because at very low oil prices the absolute price differentials between feedstock and products (cf. Fig. 2) become too small to pay back the capital investment. The case of long residue fluid catalytic cracking (LR–FCC) illustrates this well as the capacity increased tremendously åfter the second oil crisis in 1979 (Fig. 3).

Today, many of the new processes being introduced are intended to enhance control of the (molecular) composition of the fuels (Table 2). Amongst these are processes such as deep hydrogenation of gas oil (the Shell middle distillates hydrogenation, SMDH, process) and manufacturing of ethers as gasoline extender. These processes are being driven mainly by the environmental concerns regarding emissions.

Finally, in Table 2 the manufacturing of synthetic fuels is considered from a variety of sources with a prime example being the Shell middle distillate synthesis (SMDS) in which natural gas is converted to middle distillates. For such processes, crude oil prices of 20 US$/barrel are required for economic feasibility.

Table 1
Survey of transportation fuels

Fuel	World demand - 1993 (Mt/a)	Boiling range (°C)	Key property	Main processes
Gasoline	750	< 200	Octane number	Catalytic reforming, FCC, Alkylation
Kerosene	210	200–250	Smoke point	SR (HDS), HC
Diesel	460	250–350	Cetane number	SR (HDS), HC

FCC = fluid catalytic cracking, SR = straight run, HDS = hydrodesulfurisation, HC = hydrocracking.

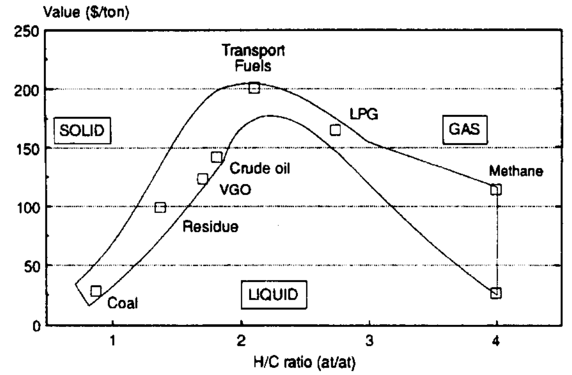

Fig. 2. Market value in 1992 of hydrocarbon fuels (VGO = vacuum gas oil; LPG = liquefied petroleum gas).

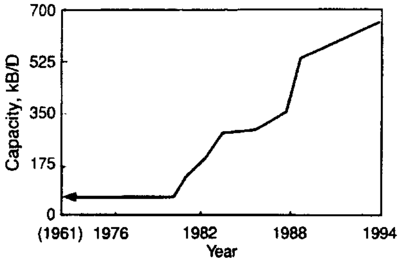

Fig. 3. Worldwide capacity of 'grassroots' residue FCC units [1].

Table 2
Transportation fuel manufacture — Generations of catalytic technology

Objective	Examples	Break even oil price ($/bbl)
Product quality	HDS	–
	Catalytic reforming	–
Product state	LR-FCC	10–20
	Hycon	10–20
	Alkylation	10–20
Product composition		
- Deep HDS/HDA	SMDH	
- Ethers	Butene isomerisation	
- *iso*-Alkanes	Alkylation	
Synfuels/biofuels		> 20
- Natural gas	SMDS	25
- Coal		40
- Biomas	(HTU)	45

HDS = hydrodesulfurisation, LR-FCC = long residue FCC, Hycon = residue hydroconversion [2], HDA = hydrodearomatisation; SMDH = Shell middle distillate hydrogenation [3], SMDS = Shell middle distillate synthesis [4], HTU = Hydrothermal upgrading [5].

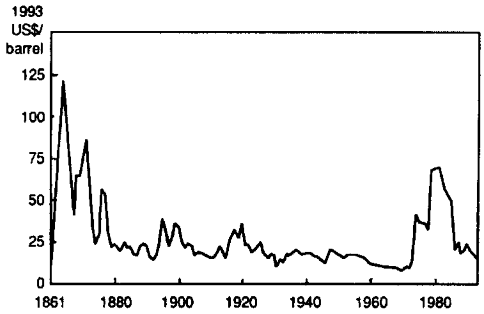

Fig. 4. Crude oil prices, 1861 to present.

An inspection of oil prices over the last twenty years indicates that the current level of 15–18 US$/barrel could be exceeded in the near future. When a longer period of time is considered (Fig. 4), however, there is as a basis for predicting a future period of low oil prices. Whatever the case, there will be an overall trend from oil refining to oil conversion and further to synthetic fuels or fuel components (e.g., methyl tertiary butyl ether, MTBE).

An important aspect of energy conversion processes is the thermal efficiency, which is defined as the heat of combustion of the products divided by that of (all) the feedstock used. Table 3 shows some typical figures demonstrating a lowering from 90% (oil refining) to 67% (methanol synthesis).

This paper deals with two aspects: (1) principles for efficient energy conversion processes and (2) new developments and future challenges for catalytic processes.

Table 3
Thermal efficiencies of energy conversion processes

Operation/product	Efficiency (% LHV of feedstock)
Oil refinery [a]	90
MTBE [b]	80
Methanol [c]	67

LHV = lower heating value.
[a] Refinery including FCC unit.
[b] From butanes and natural gas (via methanol).
[c] From natural gas.

2. Principles for efficient processes

2.1. Minimising the difference in the hydrogen content between feed and product

The first and most important step in designing an efficient process lies in a judicious selection of product and feedstock. If as an example the conversion of natural gas (mainly methane) to liquid transportation fuels is taken, the maximum thermal efficiency that can be achieved in the hypothetical process decreases with decreasing hydrogen content of the product (Fig. 5). Therefore, it follows that production of hydrogen-rich paraffinic middle distillates is more attractive from an efficiency point of view than hydrogen-poor aromatic gasoline. This aspect has been important in designing the previously mentioned SMDS process. Note that for natural gas conversion there is no difference between direct and indirect (via synthesis gas) routes as far as the theoretical maximum efficiency is concerned. For coal to synfuels, the routes via synthesis gas are less efficient on the basis of the first law of thermodynamics than direct (hydrogenation) routes. Furthermore, there is some preference for hydrogen-poor products (Fig. 5).

Besides thermodynamic considerations, there are also related economic arguments to limit the differential of the hydrogen content of feed and product. Weisz [6] has indicated that capital investment rises when more hydrogen has to be added to a heavy oil fraction or to coal. A downward trend between capital investment (per unit of energy in the product) and the overall thermal efficiency can thus be expected, which is substantiated in Fig. 6 for a large variety of conversion processes starting from coal, oil or gas to make transport fuels, methanol or lower olefins.

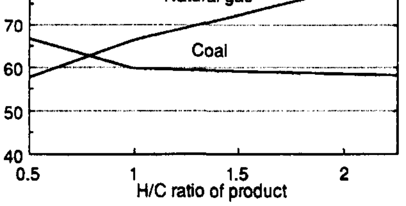

Fig. 5. Maximum thermal efficiency for synthetic fuels: synthesis gas to hydrocarbons.

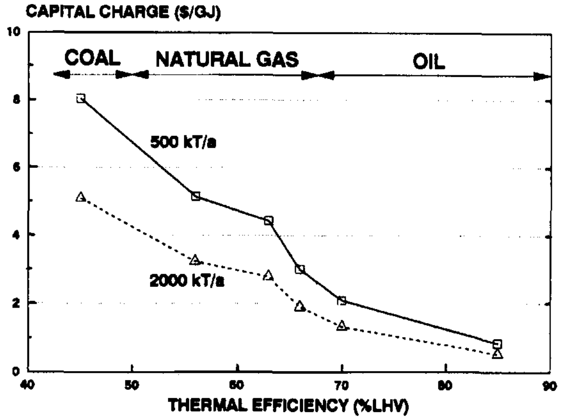

Fig. 6. Capital charge per unit of energy in product; energy carriers produced from coal, natural gas (both via synthesis gas) or oil. The specific capital is shown for two production capacities.

2.2. Minimising the number of process steps

Selection of feed and product often fixes the number of process steps involved. Consider the manufacturing of MTBE from a variety of feedstocks (Table 4). Direct etherification of isobutene with methanol involves one step, skeletal isomerisation of n-butenes to isobutene followed by etherification involves two steps

Table 4
Energy use in MTBE manufacturing

Process/feedstok	Process/name	Energy consumed (GJ/t MTBE)
iso-C_4^{2-} + MeOH → MTBE	Etherification	< 0.1
n-C_4^{2-} + MeOH → MTBE	Isomerisation	1.9
n-C_4^0 + MeOH → MTBE + H_2	Dehydrogenation	5.5

See text for explanation. C_4^{2-} = butene, C_4^0 = butane, MeOH = methanol.
Energy consumptions excluding low-pressure steam; data from [7].

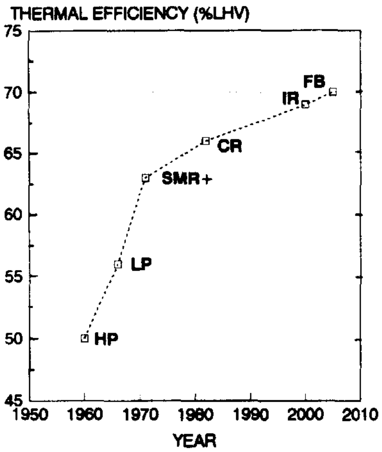

Fig. 7. The evolution of the thermal efficiency of the methanol synthesis process. HP = high-pressure synthesis; LP = low-pressure synthesis; SMR + = improved steam methane reforming; CR = combined reforming; IR = internal reforming; FB = fluid bed synthesis. Data from [8–10].

whereas, in starting from butanes, three process steps are required, viz. isomerisation, dehydrogenation and etherification. From the data summarised in Table 4, a strong increase in the amount of energy consumed to run these processes is apparent. There is, thus, an incentive to use the more readily available butenes to manufacture MTBE. The new technology to isomerise normal butenes to isobutene is of importance to open up one of the low-energy routes to MTBE.

Note that this minimisation of process steps only holds when (catalytic) routes of comparable conversion efficiency and selectivity are available. For example, for the manufacturing of methanol from methane, the preference for multiple process steps (via synthesis gas) stems from the very low yield per pass for the single-step direct route.

2.3. Improving the process continuously

Processes are improved over the years in many different ways, leading to more efficient processes. Improved catalysts allowing higher conversions per pass and/or better selectivities, intensified heat recoveries and improved process integration may serve as examples here. This suggests that there is no such thing as 'mature technology', which only occurs when further improvements are not pursued.

Methanol synthesis, as part of the process for the manufacturing of MTBE, is taken here as an example. The improvements over the years both in the synthesis step (high to low pressure) as well as in the manufacturing of the synthesis gas make the track record for this technology impressive (Fig. 7). Tentatively, possible future developments bringing the efficiency to about 70% is plotted, i.e., integrated reforming for the

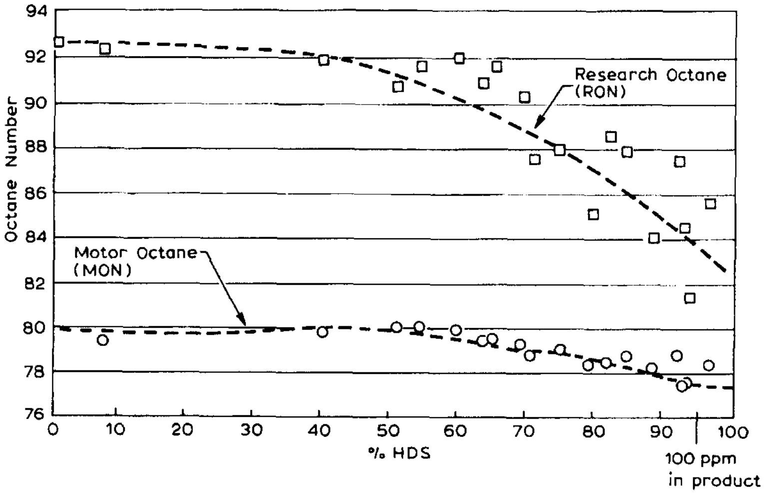

Fig. 8. Hydrodesulfurisation of FCC gasoline: octane loss versus extent of sulfur removal.

manufacturing of synthesis gas [9] and fluid bed methanol synthesis [10]. The technological hurdles to be taken for these new developments are significant, viz. materials problems in the integrated reforming and scale up of the high-pressure fluid bed reactor.

3. New developments and future challenges

A number of conversions call for further improvements of existing processes or require radically new approaches. Returning to the four generations of fuel manufacturing technology (Table 2), significant improvements are both possible and needed for all of them.

In refining-type processes, there is a need for improved HDS catalysts and processes. For diesel, legislation calls for ever-decreasing sulfur levels which is one of the driving forces to produce more active HDS catalysts, but new processes will be required as well. The sulfur removal from gasoline originating from the FCC process via conventional HDS leads to dramatic loss of octane quality (RON), as demonstrated in Fig. 8. The loss of RON relates to saturation of the olefins to low-octane paraffins. A new proposal [11] is to combine HDS with cracking of the (normal) paraffins to C_3/C_4 paraffins, thus, leading to considerable yield loss (5–15 vol.-%). Improved methods to lower sulfur while maintaining octane quality and gasoline volume are clearly needed.

Another example is catalytic reforming to produce high-octane gasoline from low-sulfur naphtha. Depending on the type of technology applied — fixed bed semi-regenerative or continuous reforming with a moving bed reactor — liquid yields currently range from 80 to 90 vol.-%. An analysis of the reforming reactions (dehydrogenation of naphthenes, paraffin cyclisation, isomerisation of paraffins and naphthenes, cracking) shows that paraffin cyclisation, is a difficult reaction and probably slow. For some time, it has been known that highly dispersed platinum on neutral or basic zeolites are very effective paraffin cyclisation/aromatisation catalysts [12]. Higher liquid yields in catalytic reforming might therefore be expected. Two drawbacks of these catalysts have up till now made commercial application for gasoline manufacturing impossible, viz. their sulfur sensitivity and the tendency to dealkylate the aromatics formed, thus, giving rise to formation of large amounts of benzene. The latter two aspects need to be improved.

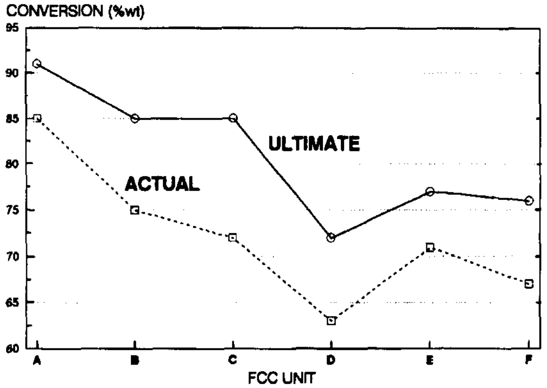

Fig. 9. Ultimate versus actual conversion of feedstock to gasoline and gases for a series of residual FCC units [13].

The FCC process is the most important for the production of gasoline. Here, the increase of gasoline yield from a given feedstock can and must be increased. The potential is illustrated by comparing the actual and maximum yield (Fig. 9) which shows that 5%–10% weight-on-feed more gasoline is still 'on the table' [13]. Improving catalyst, process and engineering options will all be needed to achieve these maximal yields.

The upgrading of gaseous components (LPG) to high-quality gasoline occurs in the alkylation process. Specifically, isobutane and butenes are coupled to trimethylpentanes (alkylate). The growing demand for alkylate is due to its low sulfur content, low volatility and high octane quality. Per unit of product in the conventional oil refinery, however, the production costs of alkylate are the highest of the gasoline pool components. In addition, the current processes make use of liquid acids (HF, H_2SO_4) which require extensive safety measures, thus, further increasing costs. All in all, the call for an alternative process based on an intrinsically safe catalyst with potential for lower production costs than the current technologies is increasing. Several new developments have been initiated, a summary of which is given in Table 5. Surprisingly, all of the industrial initiatives tabled still make use of halogen containing acids which might still give safety problems (corrosion and toxicity). Within the academical world [15,16], the emphasis has been on the use of zeolites, unfortunately with little success. It is advocated to focus on the use of oxidic solid acids whilst properly addressing integrated process aspects to enhance the chance of success.

Finally, the skeletal isomerisation of olefins to produce enhanced amounts of feedstock for ether manufacturing is discussed. The economic and environmental (energy efficiency) benefits of this technology have been discussed in Section 2.2. Over the last few years, there has been enormous progress in this area. For the reaction to convert n-butenes into isobutene, amorphous catalyst were until recently used at reaction temperatures around 450°C with lifetimes of 10 h. Today, processes are under development that apply molecular sieves operating around 350°C and lifetimes of hundreds of hours (Table 6). The zeolite ferrierite as a catalyst [17] is a leading example in this respect with commercialisation of the technology by Lyondell/CD Tech. For future research, isomerisation at 250°C is the challenge which — based on thermodynamics — enables once-through yields of 60% (Table 6). This high yield, accompanied by a reduction of the energy consumption, would even further increase the economic attractiveness of the process option.

Table 5
Solid acid alkylation developments

Company	Catalyst	Status
Catalytica	BF_3	7 bbl/day
Topsoe	CF_3SO_3H	0.5 bbl/day
Chevron/CRL	SbF_5	10 bbl/day
Kerr-McGee	$AlCl_3$	Bench
(Academia)	Zeolites	Laborator

Information from [14–16].

Table 6
Characteristics of butene isomerisation catalysts

Process parameter	Catalyst class		
	Amorphous	Molecular sieves	Future (targets)
Temperature (°C)	450	350	250
Butenes pressure	0.1	1	5
Catalyst lifetime (h)	10	> 100	> 1000
Isobutene yield (wof.-%)	35	45	60

4. Conclusions

The manufacturing of transportation fuels proceeds mainly through oil refining and conversion, with a growing emphasis on product composition through dedicated synthesis of fuel components (e.g., isoparaffins, ethers).

With the growing intensity of oil refining/conversion and the shift to synthetic components the energy consumption of the processes increases considerably.

Principles to reduce this energy consumption include a judicious choice of feed and product (low delta hydrogen content), a low number of process steps and continuous process/catalyst improvements.

Major new developments are needed, such as a process to reduce the sulfur level of FCC gasoline, reforming catalysts with an improved paraffin cyclisation function, improved gasoline yields from FCC, paraffin alkylation with a non-halogen containing catalyst and olefin isomerisation catalysts that are active and stable at low temperature.

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