

Pre-engine Converter

N. Y. Chen and S. J. Lucki

Mobil Research and Development Corporation
Princeton and Paulsboro Laboratories
Princeton and Paulsboro, N. J.

I. INTRODUCTION

During the past decade, efforts to reduce vehicular pollutant emission have included suggestions for the removal of lead from gasoline or for use of alternative fuels such as H₂ and low molecular weight hydrocarbons which are known to have high octane values and good burning characteristics (1), (2). Lead removal, which is already being implemented, raises the octane requirement of the fuel. The increased severity required in refining to produce such high octane gasoline decreases the gasoline yield per barrel of crude and, therefore, increases crude oil consumption and demands more refining capacity in the face of an impending energy crisis. Use of low molecular weight hydrocarbons is difficult to implement because of safety hazards and lack of nationwide storage and distribution systems.

The concept of attaching a catalytic reactor to an internal combustion engine converting liquid hydrocarbons to gaseous fuel was disclosed in a patent issued to Cook (3) in 1940. Recently, it has received some renewed attention. Newkirk *et al* (2) described their concept of an on-board production of CO₂/H₂ mixture by steam reforming of gasoline fuel. A U.S. patent was issued to W. R. Grace Company in 1972 (4) on a mobile catalytic cracking unit in conjunction with a mobile internal combustion engine. In 1973, Siemens Company (5) of Germany announced a "splitting carburetor" which breaks up gasoline and related fuels into burnable gases. The jet propulsion laboratory of NASA (6) is investigating the concept of the generation of hydrogen for use as an additive to gasoline in internal combustion engines.

While little technical data are available, these developments appear to represent different approaches of adapting established industrial catalytic processes designed for a narrow range of operating conditions to moving vehicles which must operate from idling to full throttle.

To design a reactor system capable of operating satisfactorily under full throttle conditions requires either a large reactor or an unusually active and efficient catalyst. A standard 300 cu. in. automotive engine at full throttle consumes fuel at a rate of about 10 cc/sec. If the reactor were operating at 1-2 LHSV (vol/vol/hr.), i.e., at the throughput of an average industrial reactor, the engine would require a catalyst bed volume of 18-36 liters (4.8 - 9.5 gallons) - far larger than the carburetor it replaces. The necessity of a multi-reactor system for continuous operation plus accessory devices including the fuel preheater, etc., would make the system impractically bulky and too slow to warm up. Therefore, a workable system clearly depended on the discovery of new catalysts of high activity. To reduce the size of the reactor to that of a carburetor, an increase in catalytic activity by a factor of at least 50-100 is necessary.

In addition to the problem of the catalytic reactor volume, the life of the catalyst is also of critical importance. Most industrial catalysts require periodic oxidative regeneration in a matter of minutes after operation to maintain their effectiveness. A catalytic cracking catalyst, such as that proposed in the patent issued to Grace (4), requires frequent regeneration. An example described in this patent states that with a zeolite-containing catalyst, 2% of the fuel was converted to coke in the catalytic converter. We estimate that under the proposed operating conditions, each volume of catalyst could process no more than 10 volumes of fuel before sufficient coke (20%) would have deposited on the catalyst to deactivate it. Thus, even if the catalyst were active enough to operate at 100 LHSV, no more than 6 minutes of continuous operation between oxidative regenerations would be feasible.

In this paper we present experimental studies with a catalyst that overcomes many of these limitations.

II. EXPERIMENTAL

1. Equipment

To demonstrate the performance of the new catalyst system, the catalytic reactor was attached to a standard motor knock Test Engine, Method IP44/60 (7), bypassing the carburetor. Figure 1 shows a schematic diagram of the catalytic unit. The reactor consisted of two 3/4 inch O.D. x 18 inches stainless steel cylinders mounted vertically, one on top of the other, and connected in series. The top chamber serving as the preheater contained 82 cc of 3 mm diameter glass beads; the catalyst bed (5 inches long) in the bottom chamber consisted of 24 cc of 20/30 mesh catalyst mixed with 12 cc of 8/14 mesh Vycor chips. During thermal runs, Vycor chips were substituted for the catalyst.

Both cylinders were electrically heated. Liquid fuel flow was metered with a rotameter. Air-fuel ratio was monitored by Orsat analysis of the exhaust.

2. Test Fuels

Two types of feedstocks were used: (1) an 86 research octane (R+O) and 79.5 motor octane (M+O) reformat obtained from Mobil's Paulsboro Refinery containing: 23.4 wt. % n-paraffins, 33.9% branched paraffins, 1.2% olefins, 1.0% naphthenes and 40.5% aromatics, and (2) a Kuwait naphtha of 40.5 clear motor octane (M+O).

III. RESULTS AND DISCUSSIONS

(1) Upgrading of a C₅-400°F reformat

The experiments were carried out by charging the liquid fuel stored in a pressurized reservoir (4500 cc) at 38 cc/min. continuously for about 2 hours through the catalytic converter during which time the motor octane number of the reactor effluent was determined every 30 minutes. At the end of 2 hours, the reactor was cooled to 800°F with purge nitrogen while the fuel reservoir was being refilled. The experiment was then repeated. Two catalysts were examined, viz., a

new stable zeolite catalyst (12 gms) and a commercial zeolite cracking catalyst (16 gms), which had previously been aged for 2 hours in a test described later. The feed rate corresponds to a weight hourly space velocity of 140 and 93, respectively. The reactor was maintained at between 910 and 920°F. Octane rating of the reactor effluent as a function of the cumulative on-stream time is shown in Figure 2. During the first 2 hours, the stable zeolite raised the octane number from the thermal value of 79.6 to 85 M+O. The octane dropped 2 numbers during the next two hours and maintained above 82 M+O for the next seven hours. The aged commercial zeolite catalyst, on the other hand, produced no appreciable conversion under the experimental conditions, i.e., at this high space velocity.

(2) Upgrading of a C₆-350 Kuwait naphtha

After 12 hours of operation without regeneration using reformat as the feed, the fuel was switched to the low octane virgin naphtha and the test continued over the aged stable zeolite catalyst for an additional two 2-hours runs before the experiment was terminated due to a mechanical malfunction. The result of the naphtha test is summarized in Figure 3. Shown in the same figure are the results over a fresh Durabead 8 catalyst and the thermal run. It is interesting to note that a boost of 22 motor octane numbers was registered by the aged stable zeolite catalyst while the fresh commercial zeolite cracking catalyst and the thermal run recorded a gain of only 10 and 6 numbers, respectively.

(3) Shape Selective Cracking

In addition to their excellent burning qualities, i.e., non-polluting combustion, light hydrocarbons have volume blending octane ratings ranged between 100 and 150 research clear numbers (R+O). Thus low octane liquids such as virgin naphtha and mildly reformed reformat can be upgraded by partially converting them to light hydrocarbons in the pre-engine converter, and feeding the entire reactor effluent directly into the engine.

A typical distribution of reaction products is shown in Table I for three samples collected when a blend of C₆ hydrocarbons was passed over the stable zeolite catalyst at 1 atm. and 900°F. The results clearly show that the catalyst exhibited preferential shape selective cracking in the order of n- > monomethyl- > dimethyl-paraffins. Thus isomers having the lower octane ratings are preferentially cracked. The C₄ minus cracked products are highly olefinic and some C₇⁺ aromatics are formed by secondary reactions.

The added advantage of shape selective cracking in the order of octane rating is illustrated by the cracking of a 61 research octane Udex raffinate, a low octane product from the solvent extraction of aromatics from a reformat. In Figure 4, curve I shows the calculated octane number of the reactor effluent vs. wt. % liquid cracked to C₄⁻ light hydrocarbons. To produce a 91 R+O fuel, about 49% of the liquid is cracked. Examination of the composition of the raffinate shows that the straight chain paraffins having an average octane rating of 17 R+O represent 27% of the liquid. Curve II shows that when these n-paraffins are selectively cracked, the octane rating of the fuel can be boosted to ~ 90 R+O with only 27% conversion. An ideal shape selective cracking

would yield curve III which represents the most efficient route of upgrading. The octane rating of the fuel is boosted to 100 R+O with less than 40% conversion.

(4) Catalyst life and stability toward oxidative regeneration

Preliminary data obtained in bench scale micro-reactor (8) studies using the reformat over both the fresh catalysts and the regenerated catalysts showed that the catalyst was stable toward air regeneration and catalyst activity was restored after regeneration. At 100 WHSV, the catalyst appeared to have a useful cycle life of about 7 hours, corresponding to processing 700 pounds of fuel per pound of catalyst. At lower space velocities, the cycle life appeared to be much longer than 7 hours, although the amount of fuel processed over the same length of operating hours was less than that at 100 WHSV.

IV. CONCLUSIONS

A highly active, stable and shape selective zeolite cracking catalyst overcomes a major problem in the application of the concept of pre-engine conversion to a moving vehicle. The catalyst is active enough to operate at above 100 LHSV and 900°F. The volume of a catalyst bed for a 300 cu. in. engine capable of operating satisfactorily at full throttle would be less than 360 cc - a manageable volume from both size and warm-up considerations. The catalyst has the capacity of processing more than 700 volumes of fuel per volume of catalyst. For a 360 cc catalyst bed, this corresponds to processing 66.5 gallons of fuel or about a driving range of 800 to 1000 miles before air regeneration would be necessary. The catalyst appears stable toward oxidative regeneration and its catalytic activity can be fully restored. Since the required volume of catalyst bed is small enough, segmented or multiple reactors could be used to accomplish cracking operation and regeneration at all times.

LITERATURE CITED

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TABLE I
Product Distribution at 900°F

Wt. %	Feed	WHSV			% Conversion		
		55	100	200	55	100	200
Methane	--	0.6	0.4	0.2			
Ethane, Ethene	--	3.3	2.5	0.8			
Propane	--	9.7	6.1	1.1			
Propene	--	7.0	5.8	3.6			
Butanes	--	2.1	1.5	0.3			
Butenes	--	3.1	2.6	2.0			
2,2-Dimethylbutane	9.1	8.6	8.6	8.6	5.5	5.5	5.5
2,3-Dimethylbutane	5.4	5.4	5.4	5.4	0.0	0.0	0.0
2-Methylpentane	13.5	8.5	10.7	11.7	37.0	20.7	13.3
Hexane, 1-hexene	24.5	6.9	10.4	16.1	71.8	57.6	34.3
Benzene	47.5	38.1	40.8	44.4	19.8	14.1	6.5
C ₇ ⁺ Aromatics	--	6.7	5.1	5.6			
R+O	77.1	96.8	92.0	84.5			
ΔON	--	19.7	14.9	7.4			
C ₄ ⁻ % Conversion	--	25.8	18.9	8.0			
ΔON/ % Conversion	--	0.76	0.79	0.93			

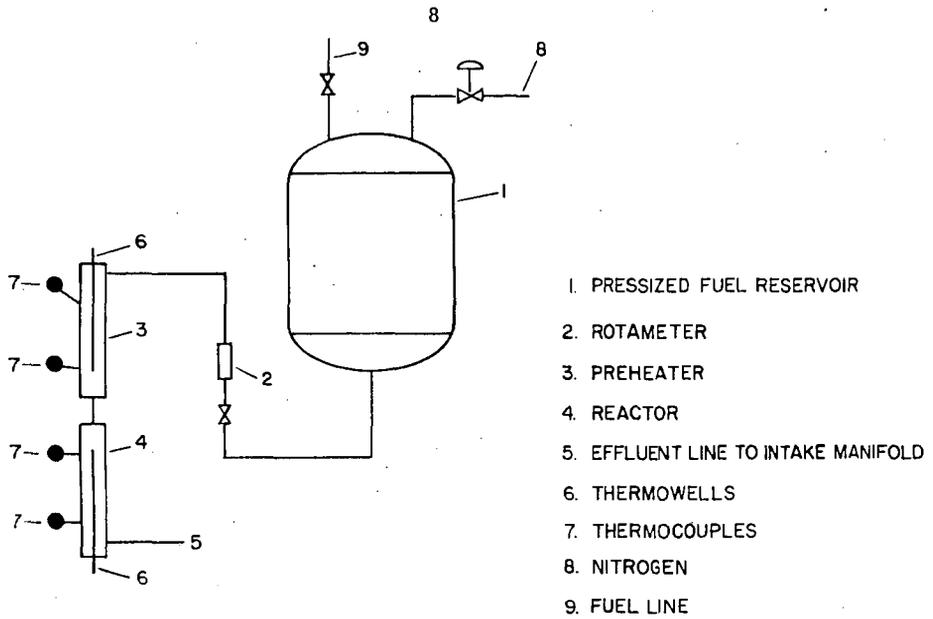


Fig. 1 SCHEMATIC DIAGRAM OF UNIT

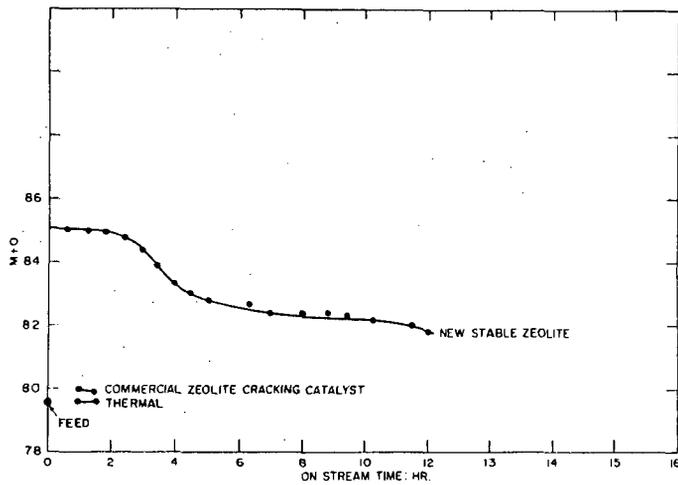


Fig 2 EFFECT OF ON STREAM TIME ON OCTANE RATING - KNOCK TEST ENGINE
 79.5 M+O C₂-400 REFORMATE
 915°F 95 LHSV

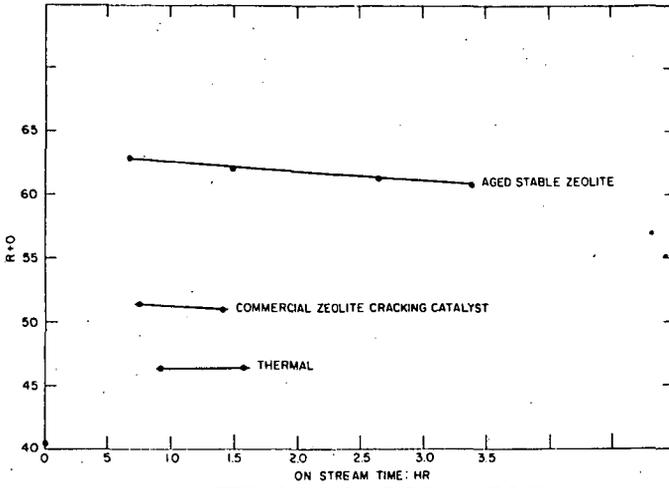


Fig 3 EFFECT OF ON STREAM TIME ON OCTANE RATING
 405 M+O KUWAIT NAPHTHA
 915°F 95 LHSV

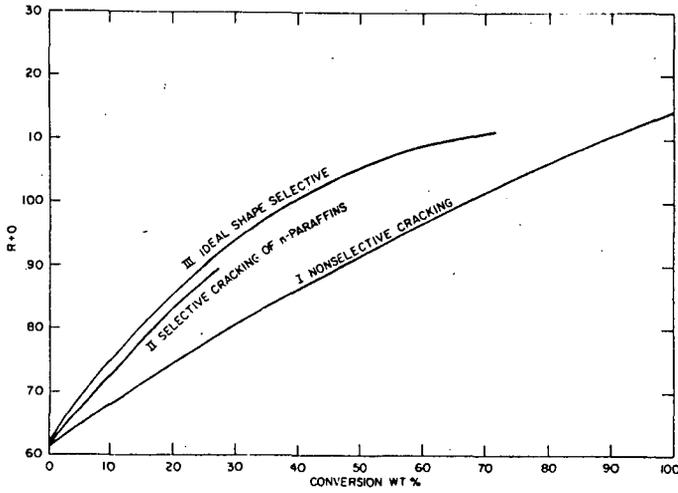


Fig 4 OCTANE RATING vs. CONVERSION LEVEL