EVALUATION OF SYNTHESIS GAS BASED HIGH OCTANE OXYGENATES (The Mixed Alcohols Option)

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OBJECTIVE: This paper presents an evaluation of synthesis gas based oxygenated fuels with particular emphasis on emerging mixed alcohols processes as options for curbing air pollution, and as motor fuel extenders and octane enhancers.

TECHNICAL APPROACH: The octane market is analyzed to estimate the expected market share of oxygenates in general and the mixed alcohols share in particular. Comparative techno-economic evaluation of the emerging processes for the direct selective conversion of synthesis gas to mixed alcohols (C1 to C6) was conducted to identify those processes that are currently ready for commercialization.

SIGNIFICANT ACCOMPLISHMENTS: Analysis indicates that there are more than 2 billion octane barrels of market available for mixed alcohols and other oxygenates by 1988 and beyond. Two European processes are currently ready for commercialization. One is the Italian "MAS" process developed by Snamprogetti using a high pressure (about 2000 psi) modified methanol synthesis catalyst. The other is the "Octamix" process developed by Lurgi in West Germany using a low (1000 psi) pressure modified methanol synthesis catalyst. Heterogeneous, low temperature modified methanol synthesis catalysts seem to be the recommended route for future catalyst development efforts to produce synthetic mixed alcohols. A similar route could be examined for the production of mixed ethers that could be used to produce a fungible high octane gasoline blends.

PUBLICATIONS: A Draft MITRE Report: WP88W00062 entitled "Evaluation of Mixed Alcohols Production Processes and Catalysts," May 1988 (currently under review at SANDIA and DOE).

INTRODUCTION

This paper presents a critical status review of mixed alcohols as a non-petroleum base alternative transportation fuel option. The main objectives are to analyze the octane market needs, evaluate the emerging technologies that are available to meet these needs and to examine the future trends and recommend areas for future research.

Three major needs have motivated the United States interest in non-petroleum based alternative transportation fuels. These needs are (1) the need to curb air pollution by reducing the carbon monoxide (CO) and ozone (smog) to their allowable ambient air quality limits, (2) the need to fill the octane gap resulting from the phasing out of toxic lead alkyls as octane enhancers, and (3) the need for at least a partial replacement of the current U.S. petroleum based transportation fuel in an attempt to reduce our trade deficit and ensure our national security and energy independence.

Various options are available to satisfy all or part of the previous needs both within the refinery and from external sources. Within the refinery there is the possibility of upgrading the main components of the gasoline pool to increase their octane levels. This upgrading is possible by changing the operating conditions, the modification of existing units, or the addition of new octane enhancement processes such as Cyclar to aromatize the LPG Stream or the Hexall to isomerize the propylenes coming out of the FCC unit. All these refinery options will add octane primarily by increasing the aromatic (BTX) content of the gasoline. Some of these aromatics are known carcinogenes and health hazards. Aromatics are also photochemically reactive and may, therefore, adversely affect the ozone level. In fact, the U.S. Environmental Protection Agency (EPA) may eventually move to limit the use of aromatics as a gasoline component. The other options used by the refiner as octane enhancers are ethanol, methanol and other methanol-based oxygenates such as methyl tertiary butyl ether (MTBE). Of these options, ethanol is limited in supply by seasonal demand on corn syrup sweetners for soft drinks, as well as by any shift in political support or phasing out of federal and/or state tax incentives. Other methanol-based oxygenates such as MTBE are also constrained by shortages in isobutylene production capacity and possible fluctuations in petrochemical product demand which represents a more profitable outlet for isobutylenes. The main sources of isobutylene are steam crackers (olefin plants) and fluxidized bed catalytic crackers (FCC). All the steam crakers of isobutylene are already committed to MTBE manufacture. If economics are favorable, a sizeable amount of the refinery isobutylene from FCC could also be made available for the production of MTBE. But, there is a limit to the amount of isobutylene that could be obtained from FCC units without significant reduction in refinery output and serious imbalance in refinery product-slate. On the other hand, methanol is not supply limited. Moreover, methanol is relatively cheap, and has a high octane blending

number (120). However, because of its various problems such as low water tolerance, lack of fungibility, drivability demerits and material incompatibility, EPA does not allow the use of methanol alone as a gasoline blending agent. It has to be used with other higher alcohols as cosolvents. A product mix which is known as "mixed alcohols."

So far, such an alcohol mix has been produced by physical mixing of the methanol with various higher alcohols in predetermined proportions. This approach involves many logistic and quality control problems to maintain a reproducible product of fixed composition. A better approach may be the direct synthesis of mixed alcohols from synthesis gas.

AVAILABLE MIXED ALCOHOL PRODUCTION PROCESSES

There are four processes for the direct synthesis of mixed alcohol from synthesis gas (Syngas). These include three European Processes and one American.

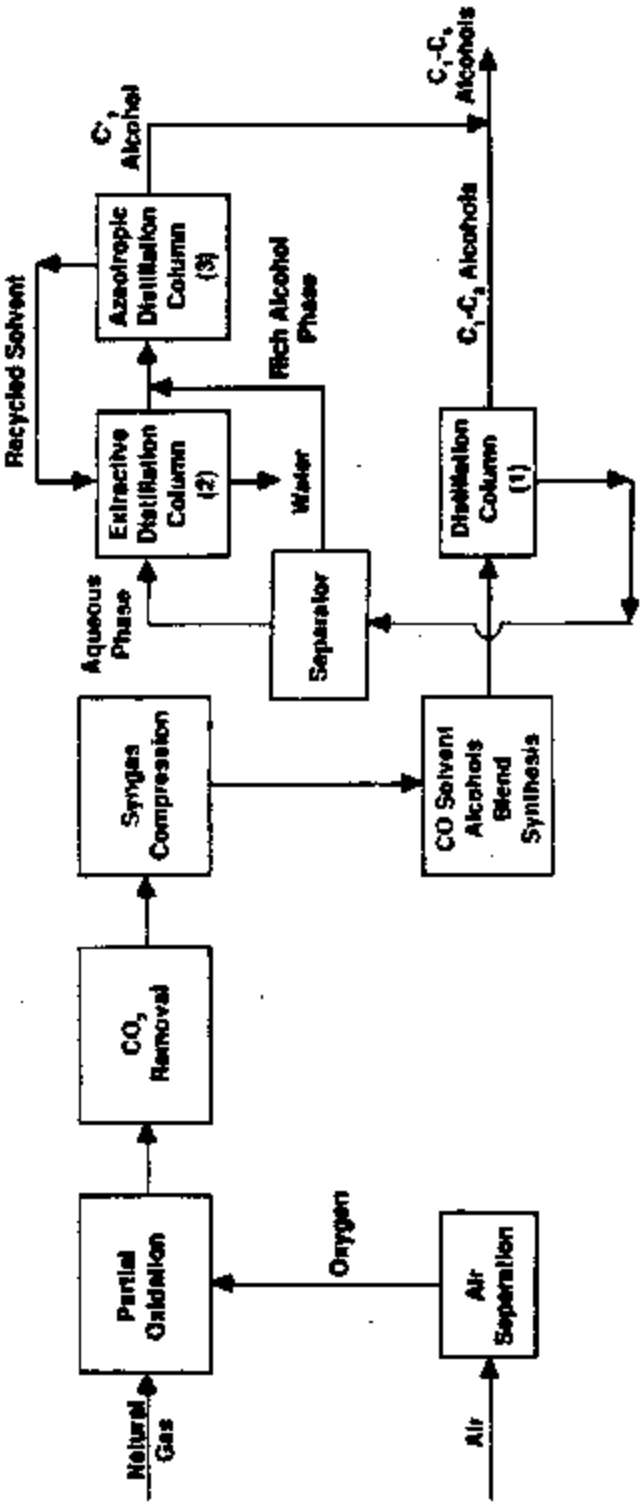
All these processes are basically similar to I.C.I.'s or Lurgi's conventional methanol production processes. They typically include an alcohol synthesis loop integrated with a product separation and purification (or water removal) sections.

A generic mixed alcohol process flow diagram is shown in Figure 1. Of particular interest in this chart is the crude mixed alcohol product separation and purification sections which involve conventional distillation, extractive distillation and azeotropic distillation in three separate distillation columns designated as column (1), (2) and (3).

In column (1), the methanol and ethanol are removed as overhead products, and the bottom stream is fed to a separator where it is separated into 2 phases: a water-rich aqueous phase, and an alcohol-rich organic phase. The aqueous phase is typically stripped (extracted) with glycol in the extractive distillation column (2) to recover the C_{3+} alcohol stream as an overhead product from the water which is withdrawn at the bottom as a waste stream. The alcohol-rich phase then undergoes azeotropic distillation in column (3) where glycol is recovered as an overhead product and is recycled to the extractive distillation column. The C_{3+} alcohol is separated as a bottom stream and is added to the already separated methanol and ethanol to make up the final C_1 to C_6 mixed alcohols product.

The stoichiometry of higher alcohols production is shown in Figure 2. Examination of this figure indicates that the main by-product of this reaction may either be water or carbon dioxide depending upon the level of the water-gas shift activity of the alcohol synthesis catalyst. In all cases the reaction is highly exothermic and generates even more heat than

FIGURE 1


Natural Gas
Air
Partial Oxidation
Oxygen
Air Separation
CO_2 Removal
Syngas Compression
CO Solvent Alcohols Blend Synthesis
Aqueous Phase
Separator
Extractive Distillation Column (2)
Water
Rich Alcohol Phase
Azeotropic Distillation Column (3)
Recycled Solvent
C_1 Alcohol
Distillation Column (1)
C_1-C_3 Alcohols
C_1-C_3 Alcohols

METHANOL

$CO + 2H_2 \rightarrow CH_3OH$ H = -21.7 KCal/Mole

$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$ H = -12.8 KCal/Mole

HIGHER ALCOHOL

$nCO + 2nH_2 \rightarrow C_nH_{2n+1}OH + H_2O$ H = -61.2 KCal/Mole (for n = 2)

$(2n-1)CO + (n+1)H_2 \rightarrow C_nH_{2n+1}OH + (n-1)CO_2$ H = -71.0 KCal/Mole (for n = 2)

WATER-GAS SHIFT

$CO + H_2O \rightarrow CO_2 + H_2$ H = -7.9 KCal/Mole

FIGURE 2

the methanol synthesis reaction. The main differences between the four previously mentioned mixed alcohols processes are discussed below.

The Italian MAS process developed by Snamprogetti uses partial oxidation to produce the syngas feed to a series of fixed-bad catalytic adiabatic reactors containing an alkali-promoted zinc-chrome-based catalyst. The crude mixed alcohol product with about 20 percent water is treated in a three column distillation system to remove the water and separate methanol and higher alcohol streams. Azeotropic distillation with cyclohexane is used to separate the C_3+ alcohols.

The syngas for IFP's process is produced by steam reforming, while the alcohol synthesis takes place in multibed quench reactors packed with copper-cobalt-based catalysts. The crude mixed alcohol product undergoes distillation to remove the water. The recovered alcohols are then purified by extractive (azeotropic) distillation with diethylene glycol.

The Lurgi's Octamix Process is essentially similar to Lurgi's low pressure methanol production process. It differs mainly by the inclusion of a carbon dioxide scrubber and the installation of a stabilizer column instead of a distillation unit. A combination of steam and autothermal reforming of methane is used to produce the desired carbon rich syngas feed to a Lurgi low-pressure tubular alcohol synthesis reactor filled with a copper-zinc-based catalyst. A unique feature of the Octamix process is the low water content (1-2 percent) of the crude mixed alcohol product. This low level of water eliminates the need for azeotropic distillation and significantly simplifies the product purification scheme.

The Dow Process is a high temperature, high pressure process initially developed by the Dow Chemicals Company in the U.S. for the direct synthesis of mixed alcohol from synthesis gas using a modified Fischer-Tropsch molybdenum-based catalyst. The promotors which are used to adjust the average carbon number of the mixed alcohol product, and to increase the selectivity of the synthesis reaction, include cobalt sulfide and alkali metal salts. A key feature of the Dow process is the control of water formation within the synthesis reactor (as is the case with the Octamix process). The process was tested in two high pressure, pilot scale reactors: a fluid bed reactor and a fixed bed reactor. Each of these reactors is capable of processing one ton of synthesis gas per day. Dow has discontinued further development of the process, but such development is now being pursued at the Union Carbide Company.

The typical mixed alcohol product usually contains about seventy percent methanol with about thirty percent cosolvent (C_2+) alcohols. However the content of C_2+ alcohol may be varied by changing the operating conditions and/or the catalyst composition. In all cases the purified mixed alcohols should not contain more than 0.1 percent of water.

GENERAL COMPARISON OF MIXED ALCOHOL PROCESSES

As shown in Figure 3, the Octamix process which uses a modified low pressure methanol synthesis catalyst seems to be most advantageous for many reasons. It is ready for commercialization and has an almost water free crude Octamix product which needs no further drying. The Octamix process, therefore, has no extractive or azeotropic distillation. This is possible because the Octamix process controls the water formation within the synthesis reactor by an almost complete removal of carbon dioxide from the synthesis loop and by using a carbon monoxide rich syngas to encourage the water-gas shift reaction to proceed in the forward direction which favors the continuous water removal. The possible disadvantage of this approach for water removal is the high cost of carbon dioxide removal.

COMPARATIVE CHARACTERISTICS FOR SYNTHETIC MIXED ALCOHOL PROCESSES

The main characteristics of the various mixed alcohols processes are compared in Figure 4. This figure indicates that the Octamix process has the mildest operating conditions compared to other processes. The figure also indicates that Octamix has a better catalyst which exhibits higher productivity, higher selectivity and more stability (i.e., longer catalyst life) than the IFP, the MAS or the Dow processes.. The difference in product slate between the various processes, is basically due to differences in the catalyst composition. The Cu/Co catalyst of IFP enhances ethanol formation and hence increases the ethanol content in the final product. On-the-other hand, the modified methanol catalyst used in MAS or Octamix processes favors the formation of more methanol and butanols.

COMPARATIVE PRODUCT CHARACTERISTICS

Only processes that are ready for commercialization and that have their product tested both in the laboratory and in the field are included in Figure 5. Thus only Octamix and MAS products are compared to MTBE with methanol figures included for easy reference. As shown in Figure 5, Octamix and MAS have almost similar product characteristics. However, only the Octamix product has been tested under U.S. test conditions and is allowed by EPA for use in gasoline blends in the U.S. market. Octamix appears to be less costly and has higher blending octane and higher oxygen content that MTBE. Octamix seems, therefore, to be more economically attractive as a gasoline blendstock than MTBE. But MTBE is a fungible refinery product, and has a lower blending vapor pressure and hence a higher butane blending capacity which makes it more attractive to the refiner as a gasoline high octane oxygenate additive.

	PROCESS			
	IFP	NAS	OCTAMIX	DOW
Process Development Status	Still Under Development	Ready for Commercialization	Ready for Commercialization	Demonstrated on Bench Scale
Process Configuration				
- Azeotropic Distillation	Yes	Yes	No	No
- Water Formation Control	None	None	Yes	Yes
- Extent of CO_2 Removal	Partial	Partial	Almost Complete	Almost Complete
Product Status	Lab Tested	Lab/Field Tested	Lab/Field Tested	Lab Tested
Catalyst Type	Modified F-T	Modified HP	Modified LP MeOH	Modified F-T
Main Catalyst	Cu/Co/Al	Zn/Cr/K	Cu/ZnO/Al	MoS_2/Co/K

FIGURE 5

CHARACTERISTICS/PROCESSES	MAS	OCTAMIX	IEP	DOW
Temperature, °C	400	285	290	330
Pressure, psi	1900	1000	1200	3000
Space Velocity, h^{-1}	7000	5000	4000	5000
H_2/CO Ratio	1.5-2	0.5-1	2-2.5	0.9-1.2
CO Conversion Per Pass	14	20	13	20
Total Alcohol Selectivity, %	90	95	75	85
C_{2+} Alcohol Selectivity, %	30	33.2	32	42
Productivity, Kg/L/h	0.234	0.46	0.15	0.2
Product Slate, wt%				
Methanol	70	66.2	57.5	49
Ethanol	2	12.5	28.5	26
C_3	3	4.9	7.1	13
C_4	15	6.6	2.8	6
C_{5+}	10	9.7	2.5	5
Catalyst Life (h)	8000	over 8000	about 2000	less than 6000
Catalyst Cost $/$ft^3$	550	375	380	---
Thermal Efficiency	56	60	54	52
Net Product Cost ¢/gal	96	90	104	116

FIGURE 4

	OCTAMIX	MAS	MTBE	METHANOL
IBP/FBP, °C	64/186	63/189	55.4	65/65
Density at 15°C, kg/l	0.8078	.804	0.74	.796
R.V.P. (blending), Psi	15.14	14.85	9.3	64
Water Tolerance (-20°C) ppm	750	1000	n/a	<500
Blending Octane, AKI	109	114	106	120
Oxygen content, wt%	41	41	18.2	50

FIGURE 5

APPROXIMATE ESTIMATION OF OCTANE MARKET

Inspection of Figure 6 indicates that there is a predicted increase in both gasoline demand and quality over the period from 1987 to 2010. This is associated with an increase in demand for octane due to various reasons. One reason is that EPA has required a total phaseout of lead alkyl as a gasoline octane enhancer by 1990 and beyond. This is estimated to generate an octane demand of 0.3 octane points during that period. Another reason is that the U.S. average gasoline pool octane is expected to increase from 88.3 AKI in 1987 to 89.9 AKI* in 2010 due to increased demand on premium grade gasoline encouraged by the increased popularity of more efficient larger size cars and the aggressive octane market race between major oil companies. The shift to a high average pool octane results in an extra octane demand of 0.6 points in 1990 which goes up to 1.6 by the year 2010.

Further demand on octane is introduced in 1990 by the expected imposition, by EPA, of the first phase of a reduced volatility limit on gasoline. This first phase, to be effective by May 16, 1989 would reduce the volatility of gasoline as measured by its Reid Vapor Pressure (RVP) by 8.7 percent. This is equivalent to the removal of 154,000 barrels per day of normal butane from the gasoline pool and amounts to an additional octane demand in 1990 of 2.0 points.

In phase 2, which is scheduled to take effect in 1992, the maximum allowable RVP would be reduced by an additional 14.3 percent which corresponds to the removal of 253,126 barrels of normal butane per day from the gasoline pool. This results in an additional octane demand of about 3 points in 1992 and beyond. The total increase in octane demand in 1990 is, therefore, estimated to be 2.9 and is expected to reach 6.9 by 2010.

EXPECTED MIXED ALCOHOLS MARKET

According to UOP, 70 to 75 percent of 1990 octane demand will be filled by upgrading existing refinery units (i.e., reformers, FCC, and alkylation units). Beyond 1990, however, new process units must be added by the refiner to raise the existing units contribution to a combined total of about 77 percent of the octane demand in 1995 and beyond. The remaining octane demand is expected to be filled by the appropriately available oxygenates.

At the existing U.S. MTBE production capacity of about 80,000 (bpd) the estimated octane contribution of MTBE to the U.S. gasoline pool in 1990 is 0.29 of an octane point. With an additional 120,000 (bpd) of MTBE

*AKI = Anti-knock Index = (Motor Octane Number (MON) + Research Octane Number (RON) divided by 2 = (MON + RON/2)

YEAR	1987	1990	1995	2010
Estimated Gasoline Demand, 10^6 Bbl/day	7.04	7.12	7.40	8.22
Average Pool Octane	88.30	88.90	89.50	89.90
Octane Demand due to:				
o Lead demise		0.30	0.30	0.30
o Octane upgrade		0.60	1.20	1.60
o Reduced volatility, Phase (1)		2.00	2.00	2.00
o Reduced Volatility, Phase (2)			3.00	3.00
Total Octane Demand		2.90	6.50	6.90

FIGURE 6

Year	1990	1995	2010
Total Octane Demand	2.90	6.50	6.90
Octane Contribution of Upgrading Existing Refinery Units (Reformer, FCC, Alkylation)	2.10	2.10	2.10
Octane Contribution of New Process Units (Penex, Cont. Platforming, Cyclar)	-	2.90	3.20
Octane Contribution of MTBE at Capacity	0.29	0.66	0.66
Octane Contributor of Ethanol at Capacity	0.21	0.39	0.39
Octane Market Available for Mixed Alcohols	0.30	0.45	0.55
Mixed Alcohol 10^3 (B/D) Required to Fill Octane Demand	106.00	166.00	225.00

FIGURE 7

capacity which is expected to come on-line by 1992, the estimated octane contribution of MTBE, at capacity, in 1992 and beyond is projected to be 0.66 of an octane point.

Similarly, at 50,000 (bpd) of available ethanol capacity in 1990, the estimated octane contribution of ethanol to the U.S. gasoline pool amounts to 0.21 of an octane point. This contribution is expected to reach 0.39 of an octane point as the available ethanol capacity is increased to 91,500 (bpd) by 1995.

The balance of the total octane demand remaining after all previously mentioned contribution represents the octane market which would be available for mixed alcohols. As shown in Figure 7, this market share is equivalent to an estimated 106,000 (bpd) of mixed alcohols in 1990 and is expected to grow up to 225,000 (bpd) by 2010. Such a market share would, however, increase dramatically if EPA moves to impose a ban on the aromatics in the U.S. gasoline pool. At that time mixed alcohols could be used to replace most of the octane that is provided by both the existing and the new refinery octane equipment.

The final choice between the various octane enhancing options available to the refiner is usually based on a number of decision criteria including availability and limitations of a given octane additive as well as the octane upgrading cost of that additive. This cost is expressed in cents per octane-barrel and is determined by the equation shown in Figure 8. This equation is applied to determine the octane-barrel upgrading cost for the various oxygenates listed in Figure 9. Toluene is also included for comparison. The lower the octane upgrading cost the more attractive is the oxygenate as an octane enhancement option.

Inspection of Figure 9 indicates that Octamix at 90 cents per gallon seems to be a more attractive oxygenate additive than MTBE at its current market price of $1.00 per gallon.

FUTURE TRENDS (ETHERIFICATION OF OLEFINS)

The etherification of olefins to produce petroleum compatible (fungible) high octane ethers seems to be the trend for future research. There is currently some reported trials to produce ETBE by catalytic reaction of ethanol and isobutylene. The catalytic reaction of isobutylene with mixed alcohols to produce the corresponding mixed ether would, theoretically, appear to be even more advantageous for various reasons. One reason is that mixed ethers are multiple boiling compounds with a boiling point range as compared to a single boiling point ether. This allows the refiner more flexibility in gasoline formulation with little or no distortion in the distillation characteristics of the base gasoline.

FIGURE 8

Octane Upgrading Cost = CC-GC/CO-GO x 100 /ONB, Where

CC = Oxygenate Cost $/BBL

GC = Base Gasoline Cost $/BBL = 30.0

CO = Oxygenate Blending Octane Number

GO = Base Gasoline Blending Octane Number = 88.0

COMPONENT	COST, ¢/ONB
Lead Antiknock, Average	5.00
Processing, Low Severity	20.00
Processing, Typical Severity	26.00
Processing, High Severity	32.00
Octamix @ 90¢/gal	37.00
MAS @ 96¢/gal	39.69
Toluene @ 90¢/gal	43.30
Ethanol (With Subsidy) @ $1.09/gal	52.60
MTBE @ $1.00/gal	66.00

FIGURE 9

Another advantage is that mixed ethers have a lower RVP than either MTBE or ETBE. Mixed ethers, therefore, allow for more butane blending in premium or mid-grade gasoline and make these products more profitable. Finally, the use of mixed alcohols, which are heavier on a molar basis, to replace methanol in the etherification reaction of isobutylene would most likely result in a better yield.

CONCLUSIONS

Mixed alcohols are viable non-petroleum based options which can at least partially meet our current needs for air pollution control, fill the future octane gap and provide transportation fuel extenders. It is estimated that there is more than 106,000 (b/d) market available for mixed alcohols and other oxygenates by 1990 and beyond. The market is expected to grow significantly with any future ban on aromatics in gasoline. Despite the current and expected future demand for mixed alcohol and other oxygenates, however, there are only two European mixed alcohols processes which seem to be now ready for commercialization: the West German, Lurgi's Octamix process and the Italian Snamprogetti's MAS process. Of these two processes, only the Octamix product could currently be used in the U.S. market.

RECOMMENDATIONS

Research efforts are needed to develop a suitable low-temperature, low pressure heterogeneous catalyst for the direct synthesis of mixed alcohols from synthesis gas. Similar efforts are also needed to develop a viable olefin etherification catalyst. Both efforts could be conducted in slurry phase reactors to take advantage of the heat removal capability of these reactors. If successful the performance of these catalyst could be demonstrated on a fairly large scale using the "Laporte" slurry phase reactor facility.

ACKNOWLEDGMENT

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