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NOVEL APPROACHES TO THE PRODUCTION OF HIGHER ALCOHOLS FROM SYNTHESIS GAS

Quarterly Technical Progress Report No. 20

For The Period July 1, 1995 to September 30, 1995

Contractor

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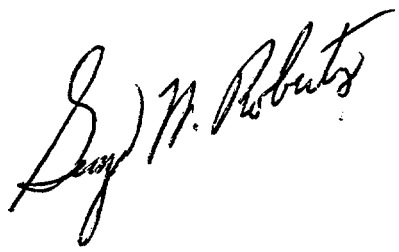

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MASTER

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CONTRACT OBJECTIVES

Task 1. Program Management.

Task 2. Liquid-Phase, Higher Alcohol Process with Recycle of Lower Alcohols.

Task 3. Novel Catalysts for Synthesis of Higher Alcohols. (Complete)

Task 4. Synthesis of Higher Alcohols via Acid-Base Catalysis. (Complete)

Task 5. Technology Evaluation. (Complete)

SUMMARY

Standard thermal stability tests were carried out on four liquids: decahydroquinoline (DHQ); 1, 3-Di-4 piperidylpropane (134PPDP), Naphthenic Base 37 and tetrahydronaphthalene (tetralin). Tetralin was more stable than decahydronaphthalene (Decalin®), and THQ was slightly less stable. Both tetralin and THQ should be evaluated further as slurry liquids in the presence of catalyst and syngas. Naphthenic Base 37 and 134PPDP do not have satisfactory thermal stability.

Vapor pressure osmometry (VPO) was shown to be an unreliable technique for measuring the average molecular weight of slurry liquids. Gas chromatography/mass spectroscopy (GC/MS) is a more accurate technique for pure compounds.

TECHNICAL DETAILS

I. Thermal Stability Tests

Activity during this quarter was devoted primarily to evaluating the thermal stability of four liquids which were considered candidates for use as slurry media for the synthesis of higher alcohols.

A. Decahydroquinoline ($C_9H_{12}N$)

Previous research has proved that Decalin® (decahydronaphthalene) has good thermal stability at reaction conditions (Temperature = 375°C, H_2 partial pressure = 68 atm). Based on the results of kinetic studies with the Engelhard "zinc chromite" catalyst, it has been hypothesized that dehydration of higher alcohols might be taking place, to form olefins and water. It is well known that hydration/dehydration reactions take place in the presence of an acidic catalyst. If an amine such as decahydroquinoline (DHQ), which should function as a base, were used as the slurry liquid, the dehydration of higher alcohols might be suppressed, making them significant products. The commercially available form of decahydroquinoline is the trans isomer, which is a liquid at room temperature (MP = -48°C) and has a slightly higher boiling point (204°C) that decahydronaphthalene (189-191°C).

An experimental program was carried out to evaluate the thermal stability of decahydroquinoline and to compare the performance of decahydroquinoline and decalin for alcohol synthesis under similar operating conditions. This program consisted of three tests:

1. - Short (1 day) stability test in the presence of catalyst

This test was carried out at 1000 psig and 375°C for 24 hrs in the presence of Engelhard Zn 0312T 1/8 "zinc chromite" catalyst. The catalyst was reduced using the procedure described in Appendix A. The test was only run for 24 hrs, instead of the standard 72 hrs, due to incorrect operating procedures, that included feeding nitrogen instead of hydrogen. Some hydrogen was detected in the gas leaving the reactor, indicating some dehydrogenation of DHQ.

A new liquid sampling system was installed in the overhead system of the stirred autoclave, which allowed samples of the vaporized and condensed slurry liquid to be collected while the unit was in operation. The samples were discolored.

2. - A two-day run with syngas in the presence of catalyst

This test was a continuation of the previous one, without shutting down the unit. The reason for continuing, even though the liquid had not been adequately evaluated, was to qualitatively determine the effect of the basic liquid on the reaction. During this test, liquid make-up was not fed to the reactor due to an operational error. This caused all the liquid to be lost from the reactor, within approximately 30 hrs of the beginning of the test. In addtion, there was a pressure drop in the reactor due to catalyst in the inlet line. After noticing the latter, the unit was shut down.

The experimental data, which is qualitative at best, suggested an increase in selectivity towards paraffins and a decrease towards olefins and oxygenates. A data summary is presented in Appendix B.

3. - A standard thermal stability test (without catalyst)

A "standard" thermal stability test was carried out. No catalyst was present. Exact conditions are shown in Appendix C.

The weight of liquid recovered at the end of the 72 hr. test was 31% less than the original charge. The appearance of the liquid changed significantly, from a clear colorless liquid to a brown, semi-waxy material with a very strong smell. The rates of light hydrocarbon (C_1-C_4) gas production were also measured. A comparison of gas production rates and liquid loss between DHQ and Decalin® is shown in Table 1. Based on these data, DHQ does not appear to be as thermally stable as Decalin.

Table 2 shows the results of gas chromatography/mass spectrometry analysis of the liquid remaining in the autoclave at the end of the thermal stability test. A substantial amount of the cis isomer formed during the TST. This isomer is a solid at room temperature, accounting for the waxy characteristic of the liquid remaining at the end of the TST.

Although the average molecular weight of the liquid did not change over the course of the TST, the gas production and liquid loss are higher than those of Decalin. DHQ should be tested in the presence of catalyst, with degradation carefully monitored.

B. 1,3-Di-4 Piperidylpropane (134PPDP)

The molecular structure and physical data for this compound are presented in Appendix D. As explained above, 134PPDP, an amine, should function as a base, possibly suppressing the dehydration of higher alcohols.

The results of the liquid stability test were not very encouraging. The weight of liquid recovered at the end of the test was 30% less than the original charge. 134PPDP is a white odorless solid at ambient temperature. The material in the autoclave at the end of the test was a black liquid at ambient temperature with a very strong smell. However, the quantity of C_1-C_4 hydrocarbons produced over the course of the test was low, as shown in Table 1.

GC/MS analysis verified the decomposition suggested by the change of appearance. Table 3 presents the analysis of the liquid at the end of the test. The resulting product is a mixture of compounds of molecular weight ranging from 98 to 189 gr/mol, with an average of 111 gr/mol. This corresponds to 47% reduction in the average molecular weight.

The GC/MS results suggest that decomposition of 134PPDP occurs mainly due to cracking of the molecule in the alkyl (propyl) bridge that connects the piperidine rings (see Appendix D), accompanied by dehydrogenation of the various piperidines to pyridines.

These results clearly indicate that this compound is not a stable liquid for the synthesis of higher alcohols.

C. Naphthenic Base 37 (NB 37)

This liquid is a Venezuelan naphthenic base used to prepare naphthenic type lubricants. The appearance of the liquid changed from clear and colorless to brown over the course of the test. The weight of liquid recovered at the end of 72 hours was 41% less than the original charge. A significant amount of C_1-C_4 gases was obtained, exceeding by two orders of magnitude the values obtained for 134PPDP at steady state and by a factor of two the maximum value for 134PPDP. This data is shown in Table 1.

Molecular weight measurement by vapor pressure osmometry (VPO) indicated a molecular weight reduction of only 4%. This reduction might be due to the cleavage of alkyl groups from the naphthenic molecules. However, as discussed below, the significance of this result is questionable. Due to the complex composition of NB37, GC/MS analysis was not considered.

These results indicate that NB37 is not a stable liquid for the synthesis of higher alcohols.

D. Tetralin (tetrahydronaphthalene)

The weight of liquid recovered at the end of the 72 hr test was 13% less than the original charge. The appearance of the liquid changed from colorless to orange-maroon. As shown in Table 1, no significant amount of C_1-C_4 gases was obtained and no significant difference between the maximum and the steady state gas make was observed.

GC/MS results for the pure and spent samples are presented in Tables 4 and 5 respectively. The concentration of tetralin in the liquid at the end of the test period was approximately 76 mol %. Although some decomposition of tetralin was observed, e.g., to butyl benzene, the majority of the loss of tetralin was to an isomer with the same molecular weight. These results were also verified by NMR spectroscopy, where spectra for both the pure and spent samples were very similar.

Although the composition of tetralin changes to some extent during the thermal stability test, this liquid is considered stable because:

- there was no reduction in average molecular weight;
- the change in composition was relatively small, and primarily due to formation of an isomer with the same molecular weight;
- gas formation was relatively low.

Table 1

Summary of the Results of Thermal Stability Tests

Liquid	Rate of C_1-C_4 gas production (% initial charge/hr)		Weight of liquid lost via C_1-C_4 gases (% of initial charge)	Total weight liquid lost (% of initial charge)
	Maximum	Steady State		
Drakeol 34	1.2	0.10	-	59
Decalin	0.095	0.0040	-	26
DHQ	0.17	0.066	5.2	31
134PPDP	0.22	0.002	1.7	30
NB37	0.42	0.13	16	41
Tetralin	0.012	0.002	0.12	13

Table 2

Composition of Spent DHQ Based on GC/MS Results

Sample: Decahydroquinoline (DHQ) after Thermal Stability Test @ 375°C (72 hr.)

Component	Retention time (min)	Probability (% accuracy)	Peak Area	Molecular Formula	MW (gr/mol)	mol%	wt%
MW 138 ?	9.61	?	127454	C8H14	138	0.5	0.5
MW 138 ?	10.44	?	239527	?	138	0.9	0.9
MW 141(*)	10.75	?	821127	C9H19N	141	3.2	3.2
trans-DHQ	**11.33**	**73**	**21444320**	**C9H17N**	**139**	**83.3**	**83.3**
cis-DHQ	**11.93**	**32**	**2861356**	**C9H17N**	**139**	**11.1**	**11.1**
THQ	12.70	69	264453	C9H11N	133	1.0	1.0
Unknowns (BP> 300°C (**)	-	-	0	-	-	0.0	0.0
Total Area			25758237			100	100
Average MW (gr/mol)					**139**		
% trans - DHQ						**83.3**	**83.3**
% of MW reduction					**none**		

(*) possibly 2-butyl quinoline.
(**) contribution of unknown components with BP>300°C assumed to be negligible.

Table 3

Composition of Spent 134 PPDP Based on GC/MS Results

Sample: 1,3-Di-4-Piperidylpropane after Thermal Stability Test @ 375°C (72 hrs)

Component	Retention time (min)	Probability (% accuracy)	Peak Area	Molecular Fomula	M W (gr/mol)	mole %
Cyclopentane, ethyl-	3.34	64	969258	C7H14	98	3.4
Pyridine, 3-methyl-	5.29	97	2892372	C6H7N	93	10.2
Nonane	5.81	83	1291130	C9H20	128	4.5
Pyridine, 4-ethyl- or	7.07	94	3192697	C7H9N	107	11.2
Pyridine, 3,4-dimethyl-		76		C7H9N	107	0.0
Pyridine, 2,4,6-trimethyl- or	8.17	62	479885	C8H11N	121	1.7
Pyridine, 3-ethyl-5-methyl-		53		C8H11N	121	0.0
Nonane, 3,7-dimethy	8.76	52	3399445	C11H24	156	11.9
Trimethylpyridine or isomer	9.22	69	617646	C8H11N	121	2.2
Hexane, 3,3-dimethyl	11.35	45	786063	C13H28	184	2.8
MW 182 ?	12.79	?	3438438	?	182	12.1
Hexylpyridine or isomer	13.72	60	2222879	C11H17N	163	7.8
MW 180 ?	14.16	?	3611994	?	180	12.7
Heptylpyridine or isomer	14.75	36	724527	?	177	2.5
Octylpyridine or isomer	16.11	?	1606058	?	191	5.6
MW 205 ?	16.65	?	575571	?	205	2.0
MW 189 ?	17.52	?	2647347	?	189	9.3
Total area			28455310			100
Average MW (gr/mol)					**111.3**	

Table 4

Composition of As-Received Tetralin Based on GC/MS Results

Component	Retention time (min)	Probability (% accuracy)	Peak Area	Molecular Fomula	MW (gr/mol)	mole %
Naphthalene, decahydro- ,trans	9.72	87	72557	C10H18	134	2.0
Naphthalene, decahydro- ,cis	10.56	91	230889	C10H12	132	6.5
TETRALIN	**11.63-11.88**	**96**	**3259926**	**C10H12**	**132**	**91.5**
Total area			3563372			100
Average MW (gr/mol)					**132.0**	

Table 5

Composition of Spent Tetralin Based on GC/MS Results

Sample: Tetralin from Thermal Stability Test @ 375°C (72 hrs)

Component	Retention time (min)	Probability (% accuracy)	Peak Area	Molecular Fomula	MW (gr/mol)		mole %
Benzene, butyl	9.79	89	2310009	C10H14	134		4.1
1H-Indene, 2,3-ihydro-1-methyl-	10.29-10.55	79	11041118	C10H12	132		19.8
TETRALIN	**11.16-11.67**	**97**	**42350560**	**C10H12**	**132**		**76.0**
Total area			55701687			100	
Average MW (gr/mol)					**132.1**		
% of TETRALIN							**76.0**

II. Vapor Phase Osmometry

The molecular weights of the four liquids discussed in Section I were also measured by vapor pressure osmometry (VPO). However, the results indicated that this type of analysis is not suitable for most of the liquids tested. Table 6 presents VPO and GC/MS results for fresh (pure) and spent samples of several liquids. The VPO results are far from the actual values for the fresh (pure) samples, whereas mass spectroscopy was very accurate for determining molecular weights of pure components.

Table 6

Comparison of Molecular Weight Measurements

	DHQ	134PPDP	NB37	Tetralin
Molecular formula	$C_9H_{17}N$	$C_{13}H_{26}N_2$	-	$C_{10}H_{12}$
Molecular weight	139	210	-	132
VPO measurement:				
Pure component	188	-	288	198
Difference (VPO - actual)	49	-	-	66
Spent Liquid (after TST*)	200	268	299	171
GC/MS measurement:				
Pure component	139	210	-	132
Difference (MS - actual)	0	0	-	0
Spent Liquid (after TST)	139	111	-	132

*TST = standard thermal stability test (see Appendix C)

Appendix A

Zinc Chromite Catalyst Reduction Procedure

(Modified for High Temperature Test)

This procedure is a combination of the method for the reduction of copper chromite catalysts suggested by Engelhard, and the procedure outlined by Tronconi, et. al. in "Synthesis of Alcohols from Carbon Oxides and Hydrogen. 4. Lumped Kinetics for the Higher Alcohol Synthesis over a Zn-Cr-K Oxide Catalyst", *Ind. Eng. Chem. Res.* **1987**, *26*, 2122-2129. Neither procedure lists a pressure for the reduction, so it was assumed to be atmospheric. Since the slurry reactor contains a liquid medium that has a characteristic vapor pressure, the reactor must be run at a total pressure at least equal to the value of that vapor pressure at the final reduction temperature, or boiling will occur and create reactor instability.

Reduction Procedure

GHSV: 5000 sl/kg cat/hr

Pressure: 1000 psig

1. Heat reactor from ambient to 130°C under nitrogen flow only (1-2 hours)
2. Start reducing gas, 5% hydrogen in nitrogen
3. Heat reactor from 130°C to 300°C under reducing gas for six hours (28.33°C/hr).
4. Change gas composition to 100% H_2 (still at 5000 GHSV).
5. Heat reactor from 300°C to 375°C for three hours (25°C/hr).
6. Hold at 375°C (Begin high temperature test)

Appendix B

Results from a two-day run with decahydroquinoline (DHQ) as a slurry medium and with the Engelhard "zinc chromite" catalyst, Zn-0312 T 1/8. The test was carried out at: T=375°C, P=2000 psig, GHSV = 5000 sl/kg cat-h, H_2/CO ratio = 0.5, Stirrer speed = 1750 rpm. The results are compared with those from a run with decalin at the same conditions with the same catalyst.

Carbon selectivity results

Component (mol %)	Decalin	DHQ	Difference
CO_2	38.6	41.7	3.1
Methane	12.0	17.5	5.5
Ethene	5.0	1.9	-3.1
Ethane	2.2	5.4	3.2
Propene	5.5	3.8	-1.7
Butene	3.2	1.8	-1.4
Methanol	23.1	20.9	-2.2
Ethanol	0.18	0.12	-0.06
Isobutanol	0.5	0.6	0.1
DME	9.9	6.4	-3.5
Total Hydrocarbons	27.9	30.4	2.5
Paraffins	14.2	22.9	8.7
Olefins	13.7	7.5	-6.2
Total oxygenates	33.7	28.0	-5.7

Appendix C

Conditions of Thermal Stability Test (TST)

Reactor Temperature:	375°C*
Reactor Pressure:	1000 psig
Length of Test:	72 hours after reaching 375°C*
Gas/Liquid Separator Temperature:	25°C
H_2 Flowrate:	3.5 sL/min.
No Catalyst Present	

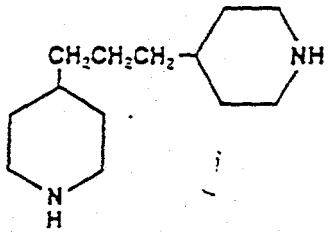
*Unless otherwise noted.

Appendix D

INDEX #3200

1,3-Di-4-PIPERIDYLPROPANE
[REILLY® DI-PIP® Amine]

C.A. 9 CI Name: Piperidine, 4, 4'-(1,3-propanediyl)bis



ASSAY: 98% minimum

Physical Constants Of The Pure Compound

Molecular Weight	210.36
Boiling Point at 760 mm Hg	329°C
Freezing Point	67.1°C
Solubility in 100 g water at 20°C	11.6 g

General Information

CAS Registry Number	16898-52-5
TSCA Inventory	Yes
EINECS	Yes
HENCS (Japan)	No