Appendix C

Denatured Ethanol

PROPOSED SPECIFICATIONS FOR DENATURED ETHANOL

A. RFA's Ethanol Producers Survey

The Renewable Fuels Association (RFA) has conducted a survey of ethanol producers within its membership. The objective of the survey was to obtain information regarding the sulfur content in denatured ethanol and certain hydrocarbons in the denaturants. The survey included forty-three companies that operated ethanol production facilities. Of the facilities surveyed, the RFA received data from twenty-seven that have a total production capacity of 1.42 billion gallons per year. The data covers production capacity representing 81 percent of the fuel ethanol production capacity in the United States. RFA presented its findings from its survey at the June 15, 2000, workshop on relating issue to the California Phase 3 reformulated gasoline regulations. A copy of the RFA's reports on the ethanol producer survey has been included as part of this appendix. Also included is the information the manufacture, properties and specifications of denatured ethanol presented by the RFA at the May 4, 2000 public workshop.

B. ASTM Specifications for Denatured Ethanol

ASTM D4806 requires that the only denaturants used for fuel ethanol shall be natural gasoline, gasoline components, or unleaded gasoline at a minimum concentration of two parts by volume per 100 parts by volume of fuel ethanol (2.0 volume percent). The use of hydrocarbons with an end point higher than 437 ^{o}F are prohibited. The denaturants permitted may be included as part of the 10 volume percent denatured fuel ethanol blended with a gasoline if they do not exceed five parts per volume 100 parts by volume (4.8 volume percent) of fuel ethanol. The use of methanol, pyrroles, turpentine, ketones and tars are prohibited. Denatured ethanol must conform to the performance requirements specified in ASTM D 4806-99.

C. Test Methods

There currently is a test method for sulfur in ethanol and no test methods for measuring benzene, olefins, or aromatics. The ARB's Monitoring & Laboratory Division (MLD) is coordinating a robin round series of tests between participating laboratories to evaluate ASTM D5453 for determining the sulfur content in denatured ethanol. It is anticipated that ASTM D5453 test method will be suitable to accurately measure the sulfur content in ethanol. However, because there are no comparable test methods applicable to measure benzene, olefins, and aromatics at the concentration levels of these compounds that are found in denatured ethanol. Therefore, it has been suggested that the concentration of these compounds in denatured ethanol will be calculated using the concentration of these compounds found in the denaturant. The test methods to be used for testing the denaturants are the ones specified in the CaRFG regulations for determining compliance. Table C-1 lists the test method currently available for determining compliance to the proposed specifications for denatured ethanol and denaturants.

Table C-1
Test Methods

Specification	Test Method
Sulfur in Ethanol	ASTM D 5453-00
Benzene in Denaturant	ASTM D 5580-00
Olefins in Denaturant	ASTM D 6550-00
Aromatics in Denaturant	ASTM D 5580-00

D. Proposed Specifications

The staff is not proposing to set a limit on the sulfur of the denaturant to provide more flexibly to the ethanol producers. The result of the RFA survey shows that the sulfur contents in undenatured ethanol ranged from 1 ppm to 11 ppm. The specifications would allow producers that have lower sulfur content in the undenatured ethanol to use denaturants with high sulfur content. Table C-2 shows what the sulfur content of denatured ethanol would be if a denaturant with 60 ppm sulfur were used to denature the ethanol.

Table C-2
Final Sulfur Levels in Denatured Ethanol
For Different Addition Levels of Denaturant

Undenatured Ethanol (Sulfur Content, ppm)	Denatured Ethanol[1] (Sulfur Content, ppm)	
	2.0% Denaturant[2]	4.8% Denaturant[2]
8	9	10
9	10	11
10	11	12
11	12	13
12	13	14
13	14	15

1. Assumes that the denaturant has a sulfur level of 60 ppm.
2. Federal regulations and ASTM standards require a minimum denaturant concentration of 2 vol.% and a maximum concentration of 4.8 vol.%

Table C-3 demonstrates that the sulfur content of the denaturant used by ethanol producers could vary widely depending upon the sulfur content of the undenatured ethanol.

Table C-3
Amount Of Sulfur in Denaturant For Different Addition Rates
Without Exceeding the 10 or 15 ppm Limit for Denatured Ethanol

Sulfur Content of Undenatured Ethanol	Sulfur Content of Denaturant to Produce a Denatured Ethanol with 10 ppm Sulfur Content		Sulfur Content of Denaturant to Produce a Denatured Ethanol with 15 ppm Sulfur Content	
	2.0% Denaturant	4.8% Denaturant	2.0% Denaturant	4.8% Denaturant
1	451	189	701	293
2	402	169	652	273
3	352	149	603	253
4	304	129	554	233
5	255	109	505	213
6	206	89	456	194
7	157	70	407	174
8	108	50	358	154
9	59	30	309	134
10	10	10	260	114
11	--	--	211	90
12	--	--	162	75
13	--	--	113	55
14	--	--	64	35
15	--	--	15	15

DENATURED FUEL ETHANOL

MANUFACTURE, PROPERTIES AND SPECIFICATIONS

PRESENTED AT THE CALIFORNIA PHASE 3
REFORMULATED GASOLINE REGULATIONS WORKSHOP

MAY 4, 2000

Carl F. Reeder

Archer Daniels Midland Co.

Chairman, Renewable Fuels Association Technical Committee

U. S. FUEL ETHANOL PRODUCTION

12 Corn Wet Milling Plants

31 Corn Dry Milling Plants

9 Other Sources (Wheat, cheese whey,

potato, beverage and wood waste)

Wet Mills - 63 % of Production

Dry Mills - 35 % of Production

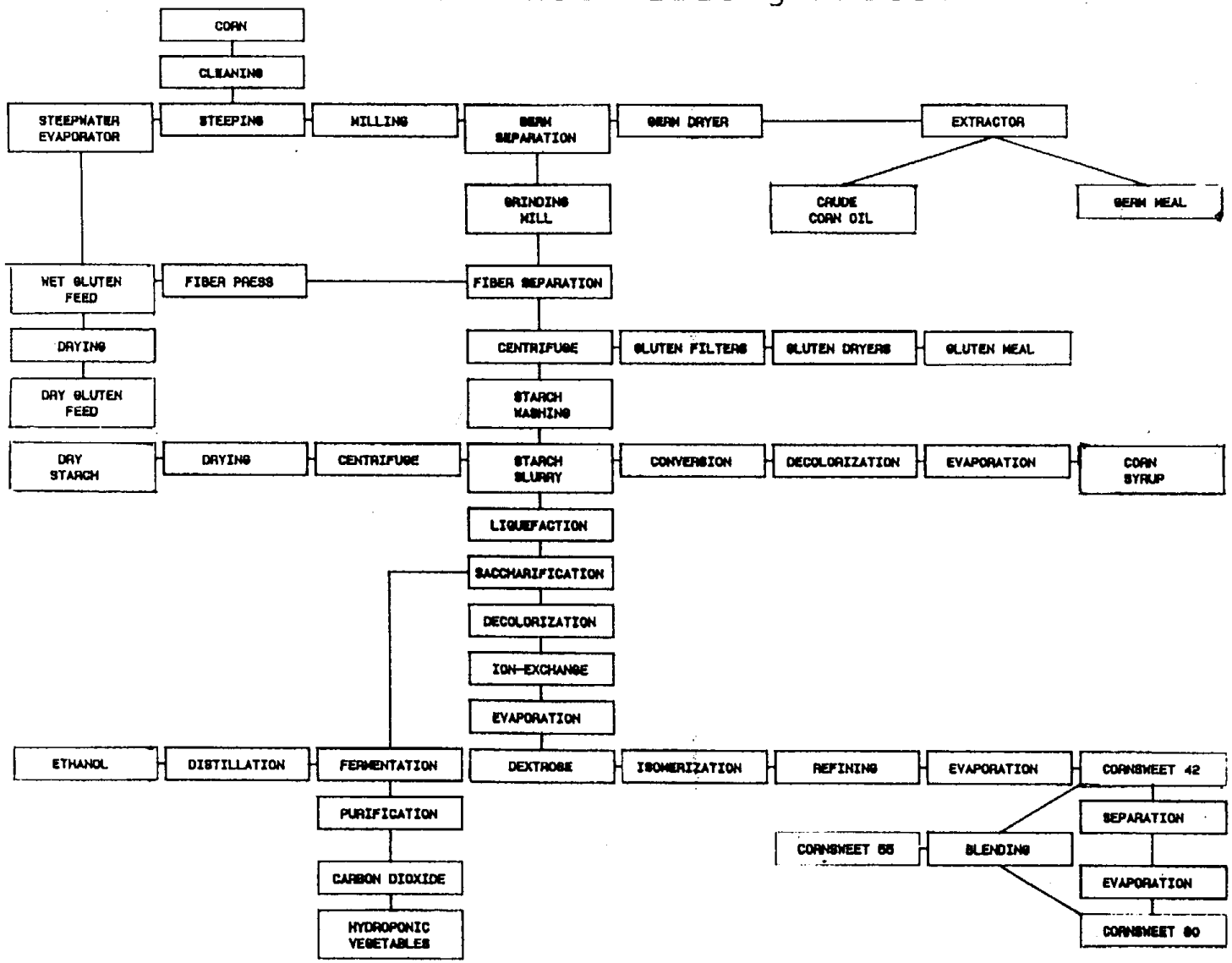
Other - 2 % of Production

SULFUR IN FUEL ETHANOL

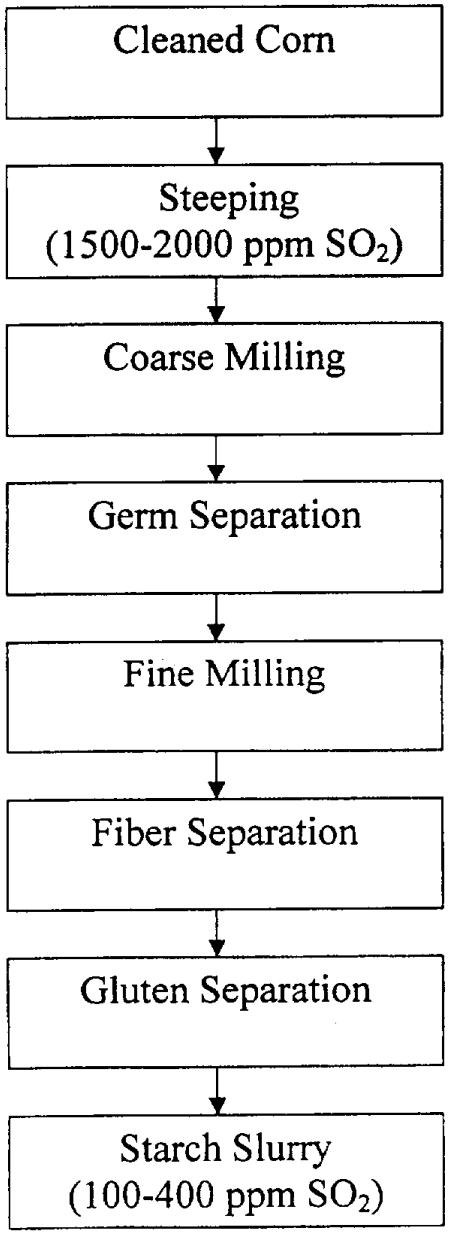
SOURCES OF SULFUR

1. Ethanol Production Process
2. Denaturant

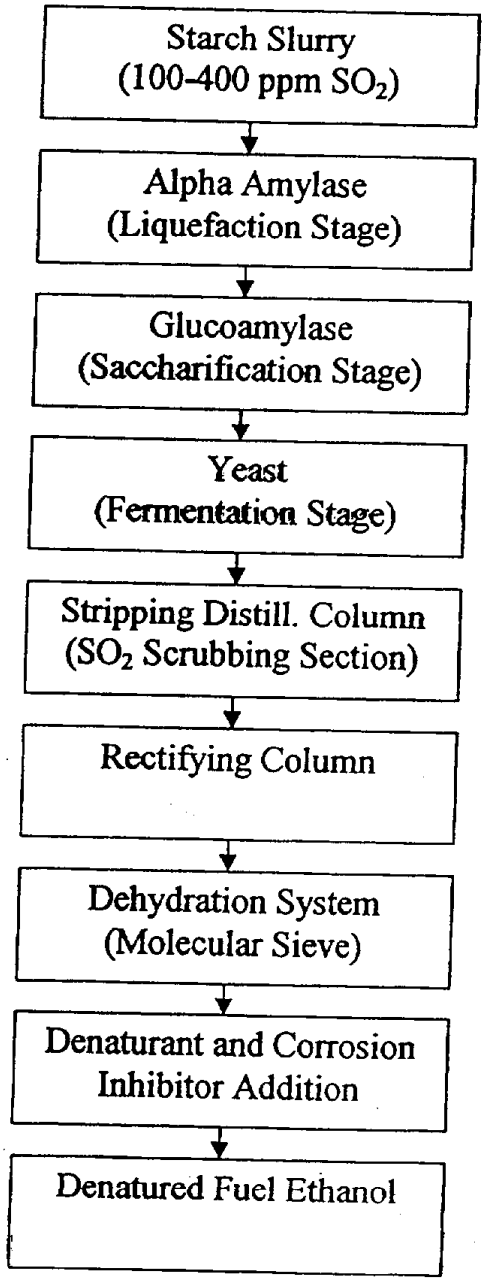
Corn Wet Milling Process



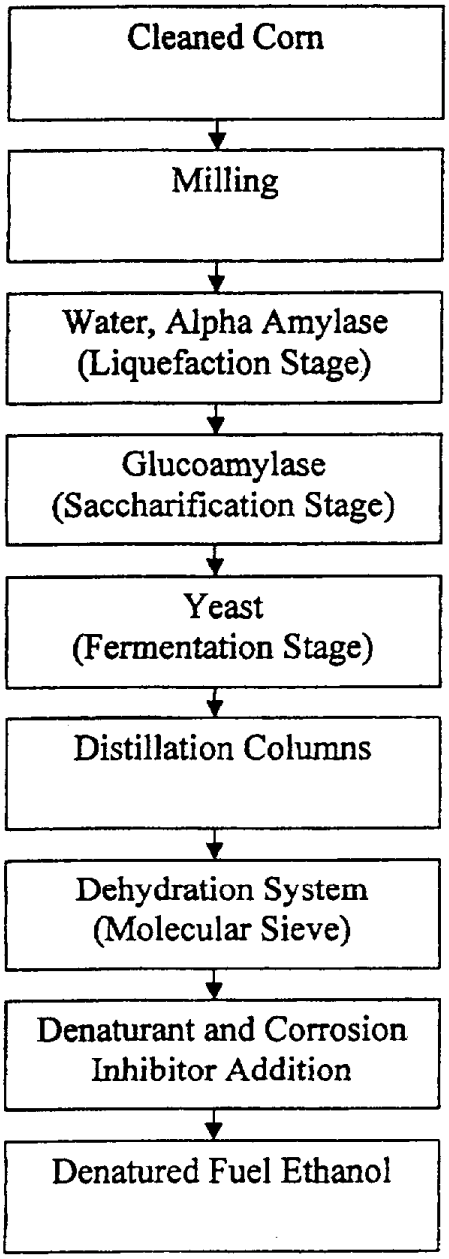
Corn Wet Milling Process



Corn Wet Milling Ethanol Process



Corn Dry Milling Ethanol Process



DENATURED FUEL ETHANOL
TYPICAL COMPOSITION

Ethanol, volume %	94.5
Other Fermentation Alcohols, volume %	0.3
Denaturant, volume %	4.6
Water, volume %	0.6
Acidity (as acetic acid) mass %	0.004
Solvent Washed Gum, mg/100mL	2
pHe	7.0
Chloride Content, mg/L, max.	2
Copper Content, mg/kg, max.	Not Detectable
Appearance	Clear and Bright
Corrosion Inhibitor	20 to 30 lbs/1000 bbl

CORROSION INHIBITOR IN DENATURED ETHANOL

The Renewable Fuels Association (RFA) recommends that all fuel ethanol producers add a corrosion inhibitor to all of their fuel ethanol production.

OBJECT: To provide corrosion protection from points of distribution and storage to final ethanol/gasoline use.

USAGE: The corrosion inhibitors approved by the RFA provide fuel ethanol a B+ or better rust rating when tested by NACE TM-01-72 method.

SUMMARY: Field surveys show that the industry is producing ethanol with virtually 100% having NACE rust ratings of A. No samples are below B+ rating.

DENATURED FUEL ETHANOL

TYPICAL PROPERTIES

Gravity, API	47.5
Specific Gravity, 60°F	0.7905
Pounds/Gal., 60°F	6.58
Vapor Pressure, 100°F, psi	4.0
Blending Vapor Pressure, 5.7 to 10% in gasoline, psi	18
Oxygen Content, wt. %	33
Color	Colorless
Appearance	Clear, Free of Suspended Matter

FUEL ETHANOL DENATURANTS

Denaturant Definition Specific to D4806 - natural gasoline, gasoline components, unleaded gasoline or toxic or noxious materials added to fuel ethanol to make it unsuitable for beverage use but not unsuitable for automotive use.

PROPERTIES OF NATURAL GASOLINE HISTORICALLY AVAILABLE FOR DENATURING OF ETHANOL

Color, Saybolt	+25 to +30
API Gravity	80 - 85
RVP @ 100°F, psi	13 - 14
Sulfur, ppm	60 - 160
Research octane number	76
Motor octane number	74
Distillation °F, Typical	
1 BP - 92	
10% - 105	
20% - 110	
50% - 125	
90% - 185	
FBP - 265	
Benzene, volume %	0.3 - 0.5
Olefins, volume %	0.1 - 0.8
Aromatics, volume %	1.0 - 2.6

FUEL ETHANOL PRODUCERS' RESPONSE TO CaRFG3 PROPOSED SPECIFICATION

1. The ARB & industry need to review test methods associated with the proposed aromatic, benzene and olefin limits.

2. The ethanol industry is anxious to work with CARB and ASTM to verify an appropriate test method for sulfur in fuel ethanol.

3. It is inappropriate for the ethanol industry to commit to a sulfur specification today. Data from the supplier survey is scattered, the test methods are not known, denaturant sulfur levels are not known and several of the producers have not responded to the survey.

4.We cannot comment today on a sulfur specification until the second RFA survey is completed. We can respond at the next CARB workshop.

REPORT ON ETHANOL PRODUCERS SURVEY

PRESENTED AT THE CALIFORNIA PHASE 3
REFORMULATED GASOLINE REGULATION WORKSHOP

JUNE 15, 2000

Carl F. Reeder

Archer Daniels Midland Co.

Chairman, Renewable Fuels Association Technical Committee

ETHANOL PRODUCERS SURVEY

Requested by the Board of Directors of the Renewable Fuels Association (RFA).

Objective: To ascertain from producer reports the sulfur content of ethanol and certain hydrocarbons in the denaturants. This information will provide a basis for responding to the establishment of specifications for fuel ethanol by regulatory agencies.

Survey conducted during May and June, 2000 by Edward D. Heffernan, General Counsel of the RFA. There is a possibility of receiving additional reports and as they are received minor modifications will be made in the data.

All data reported has remained proprietary. Test results have been reported by the producer only to Mr. Heffernan who summarized the data and reported it to the RFA office.

ETHANOL PRODUCERS SURVEY

A questionnaire was sent to 43 companies that operate single or multiple fuel ethanol plants.

The questionnaire form asked for the sulfur content of the producer's undenatured and denatured ethanol. The sulfur, benzene, olefin and aromatic content of the denaturant used by the producer was also requested.

The respondents to the survey form sent single samples of undenatured ethanol, denatured ethanol and the denaturant to independent petroleum testing laboratories for analysis.

Test results were reported by the testing laboratory to the producer who then reported them to Mr. Heffernan.

ETHANOL PRODUCERS SURVEY

Test Methods:

Sulfur in Ethanol ----------ASTM D5453

Sulfur in Denaturant ----------ASTM D2622

Benzene in Denaturant ----------ASTM D3606 or IR

Olefins in Denaturant ----------ASTM D1319

Aromatics in Denaturant ----------ASTM D5769

The information shown in the following table is based upon data received from 27 plants that have a total production capacity of 1.42 billion gal./yr. This response represents 81% of the 1.75 billion gallons of yearly production capacity of the ethanol industry.

INFORMATION REPORTED BY PRODUCERS

Information Requested	Average	Range
Sulfur content of the undenatured ethanol	2.9 ppm mass	1 –11 ppm mass
Sulfur content of the denatured ethanol	8.7 ppm mass	2.1 – 27.2 ppm mass
Sulfur content of the currently used denaturant	127.7 ppm mass	9.1-733.9 ppm mass
Benzene content of the denaturant	0.63 vol. %	0.01 - 1.94 vol. %
Olefin content of the denaturant	0.55 vol. %	0.02 – 2.1 vol. %
Aromatic content of the denaturant	1.33 vol. %	0.05 – 6.6 vol. %

Note: The above represents 81% of 1.75 billion gallons of yearly production capacity in the ethanol industry.

ETHANOL PRODUCERS SURVEY

The ethanol industry requires flexibility in the choice of denaturants. Currently nearly 100% of the denaturant used is natural gasoline. Other denaturants may be options in the future.

CaRFG3 gasoline is proposed to have a cap limit of 1.10% benzene, 10% olefins and 35% aromatics.

For producer flexibility, the benzene, olefin and aromatic limits in fuel ethanol should be set to allow for the possibility of using CaRFG3 gasoline as a denaturant.

ETHANOL PRODUCERS SURVEY

COMMENTS AND SUMMARY:

The Renewable Fuels Association has completed a survey of the U.S. fuel ethanol producers. The RFA response to proposed specifications of key properties is based upon replies from companies representing 81% of the current fuel ethanol production capacity.

The test data reported represents only one sample from each reporting producer. It is not known how much variation in the reported values there would be over a long production period.

Also, the test method for sulfur ASTM D5453, does not include ethanol in the scope of applicability. Therefore, no precision for repeatability and reproducibility has been determined for the use of this method for total sulfur content in ethanol.

CARB is considering setting a lower sulfur standard for ethanol than for gasoline on the basis that ethanol is not a motor fuel but a fuel component. However, with Ed-85, ethanol is the motor fuel and gasoline is the blend component. It is appropriate that the sulfur standard (flat limit) for ethanol be the same as the average limit for gasoline.

A degree of tolerance must be incorporated into specifications based upon the reported numbers because of the lack of analytical data on multiple production samples and lack of precision information on the D5453 test method. Uniformity of the gasoline and ethanol specifications is also a factor.

Based upon the foregoing, the RFA suggests the following specifications for fuel ethanol that is blended to produce CaRFG3 gasoline:

Sulfur, max.	15 ppm mass
Benzene, max.	0.10 vol. %
Olefins, max.	0.50 vol. %
Aromatics, max.	1.70 vol. %