THE POTENTIAL FOR ALCOHOLS AND RELATED ETHERS TO DISPLACE CONVENTIONAL GASOLINE COMPONENTS

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Abstract

The United States Department of Energy is required by law to determine the feasibility of producing sufficient replacement fuels to replace 30 percent of the projected United States consumption of motor fuels by light duty vehicles in the year 2010. Replacement fuels are non-petroleum portions of gasoline, including alcohols, natural gas and certain other components. A linear program has been used to study refinery impacts for production of "low petroleum" gasolines, which contain substantial volumes of replacement fuels. The analysis suggests that high oxygenation is the key to meeting the replacement fuel target, and major contributors to cost increase can include investment in processes to produce olefins for etherification with alcohols. High oxygenation also can increase the costs of control of vapor pressure, distillation properties, and pollutant emissions of gasolines. Year-round low petroleum gasoline with near-30 percent non-petroleum content might be produced with cost increases of 23 to 37 cents per gallon, and with substantial decreases in greenhouse gas emissions in some cases. Cost estimates are sensitive to assumptions about pollutant emissions, availability of raw materials and other issues. Reduction in crude oil use, a major objective of a low petroleum gasoline program, is 10 to 17 percent in the analysis.

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Legislative Basis for Low Petroleum Gasoline

The Energy Policy Act (EPACT) of 1992 requires the Secretary of the U.S. Department of Energy to determine the feasibility of producing and using sufficient non-petroleum fuels or fuel components to replace 30 percent of light duty motor fuels by the year 2010. EPACT also requires the Secretary to determine the greenhouse gas (GHG) emission implications of increasing the use of replacement fuels

Alternative fuels, such as ethanol, are those motor fuels that are "substantially not petroleum," being derived from sources other than crude oil. A replacement fuel is also substantially not petroleum, but it replaces only a portion of a petroleum-derived motor fuel. For example, ethanol is a replacement fuel in a gasoline containing 10 percent ethanol.

In its marriage with petroleum-derived fuels, the replacement fuel concept depends on the continuing existence and technical development of the petroleum refining infrastructure. Gasoline is the predominant fuel for light duty vehicles, and this report focuses on refinery production of "low petroleum" gasolines from alcohols and related ethers. Like all highway gasolines, low petroleum gasolines must comply with requirements of the U.S. Clean Air Act.

The Clean Air Act Amendments of 1990

The Clean Air Act Amendments of 1990 (CAAA) include programs for oxygenated gasoline and for reformulated gasoline (RFG). The oxygenated gasoline program required that, beginning November 1, 1992, gasoline with a minimum oxygen content of 2.7 weight (wt) percent must be sold during winter months in about 40 cities not in compliance with carbon monoxide standards. RFGs are required starting January 1, 1995, in nine areas with extreme or severe ozone pollution problems. RFG formula and emissions performance standards are shown in Table 1.

Emissions modeling provides a means for predicting the emissions performance of a gasoline, given other properties of the gasoline. The Complex Model of the U.S. Environmental Protection Agency (EPA) is a set of equations that predicts emissions of VOCs, TAPs, and NOx in terms of gasoline properties including RVP, E200, E300, benzene, oxygen, sulfur, aromatics, and olefins contents. The Complex Model must be used after March 1, 1997, to certify the emissions performance of gasolines.

The nine areas in the extreme and severe ozone nonattainment categories comprise about 25 percent of the U.S. gasoline market. Other areas are allowed to petition the EPA to "opt-in" to the RFG program. RFG demand in 1995 accounts for about 25 percent of total U.S. gasoline demand. Besides requiring RFG in the covered ozone nonattainment areas, the CAAA require that gasoline in all other areas not be any more polluting than it was in 1990. Without this "anti-dumping" provision, the potential exists for emissions from conventional gasoline (CG) to worsen as polluting fuel components are removed from RFG.

Table 1. Formula and Emissions Performance Standards for U.S. Reformulated Gasoline

Standard	Phase I (beginning January 1, 1995)	Phase II (beginning January 1, 2000)
Oxygen content	2 wt percent minimum	
Benzene content	1 vol percent maximum	
Additives	No additives with heavy metals	
Volatile Organic Compounds (VOCs include all oxygenated and non-oxygenated hydrocarbons except methane and ethane)	Must be reduced by at least 15 percent during summer high-ozone season, compared with the calculated VOC emissions from use of the statutory baseline gasoline.	Must be reduced during summer by 25.9 percent on a per-gallon basis or by 27.4 percent on an averaged basis.[a] A greater reduction is required in southern states.
Toxic Air Pollutants (TAPs consist of benzene, 1,3 butadiene, formaldehyde, acetaldehyde, polycyclic organics)	Must be reduced by at least 15 percent during entire year, compared with the calculated TAP emissions from use of the statutory baseline gasoline.	Must be reduced year-round by 20 percent on a per-gallon basis or by 21.5 percent on an averaged basis.
Nitrogen Oxides (NOx)	Must not increase relative to emissions of the statutory baseline gasoline.	Must be reduced during summer by 5.5 percent on a per-gallon basis or by 6.8 percent on an averaged basis. Must not increase during winter on a per-gallon basis and must be reduced by 1.5 percent on an averaged basis.

[a]For per-gallon standard, every gallon of RFG produced at the refinery must meet the same emissions-performance requirements. For averaged standard, different batches of RFG may vary within limits, but the refinery's total RFG output must satisfy the specified average emissions performance requirement.

The ORNL Refinery Yield Model

The potential for low petroleum gasoline production has been analyzed with the Oak Ridge National Laboratory Refinery Yield Model (ORNL-RYM), a refinery linear program (DOE/EIA 1984a and 1984b; Tallett 1988 and 1992). ORNL-RYM tracks octane, RVP, oxygen content, sulfur, benzene, aromatics, total olefins, distillation points, VOC, TAP, and NOx on all

gasoline component streams. In
separate data tables in ORNL-RYM, blending components for each gasoline grade are identified; blending values are assigned to over 140 components; and blending specifications are set. Properties for distillates and jet fuels are handled conceptually the same as for gasoline.

Changes in crude feedstock are described in tables for crude quantity and quality. ORNL-RYM includes 48 refining processes, which can be used to produce 40 different products from more than 100 crude oils. Individual process units can have several modes of operation, each mode with different feedstocks and yields. An investment module provides for the addition of processing capacity.

ORNL-RYM can represent various regional refining configurations. The model assumes that all refineries within a large region are interconnected. Consequently, ORNL-RYM, like most refinery linear programs, has a tendency to over-optimize when analyzing regional refinery capability. The over-optimization problem can be mitigated by focusing on changes in refining variables, rather than relying on the model to predict exact outcomes.

Representation of Non-linear Emissions Models in a Linear Program

ORNL-RYM represents gasoline blending to satisfy emissions constraints defined by EPA's Complex Model (Korotney 1992). The non-linear Complex Model presents difficult adaptation problems for use in refinery linear programs. Each gasoline blending component has VOC, TAP, and NOx blending values that vary with overall gasoline composition. The Complex Model is represented in ORNL-RYM by a linear delta method. Off-line software computes coefficients for Δemissions/Δproperty. These coefficients are then used to compute emissions blending values for the gasoline components. ORNL-RYM is solved iteratively, until convergence of the coefficients.

Premises for Low Petroleum Gasoline Study

Petroleum Administration for Defense District III (PADD III, the U.S. Gulf Coast) is the region for study of low petroleum gasoline production. It is assumed that seasonal gasoline and distillate demand will be the same as in 1989, with gasoline demand adjusted to account for fuel economy differences, and with full opt-in by ozone non-attainment areas (Warden 1992a and 1992b). RFG production is assumed to be 62 volume percent of total gasoline production. It is also assumed that 60 percent of RFG produced in PADD III will be consumed in northern areas, and 40 percent will be consumed in southern areas (NPC 1992). Total product output is fixed, except for coke and sulfur production. Crude quality is constant, with sulfur and gravity projected to be 1.6 wt percent and 32°API.

Limits on Transportation Fuel Properties

The averaged basis standards for pollutant emissions, with allowances for enforcement compliance, are used in the low petroleum cases for year 2010. Other specifications for low petroleum gasoline need to be generally compatible with the ASTM D-486 specifications. Some important considerations include (EEA):

Octane

ASTM D-486 sets an octane limit for the average of Research and Motor Octane (R+M)/2, by grade of gasoline. However, the octane sensitivity, R-M, can be an issue with some blends. The sensitivity minimum specification of 7.5 must be augmented with a maximum sensitivity specification of about 15. The maximum specification will avoid problems with knock.

Reid Vapor Pressure

RVP is a measure of gasoline volatility, and the RVP specification varies seasonally and geographically. RVP reduction is the most cost-effective mechanism for reducing VOC in summer gasolines. In many cases, RVP will be driven to a lower limit to satisfy the RFG VOC specification. The assumed lower limits are 6.5 for summer and 11.6 for winter, below which there are operability concerns because of insufficient fuel volatility.

Distillation

For the low petroleum study, the distillation temperature ranges for summer RFG have been set at the combined limits for California Phase I and Phase II RFGs. The allowable range for T50 is 200 to 230°F, and 290 to 325°F for T90. The distillation ranges for winter gasolines have been set to recently reported maximum and minimum values (NIPER 1993).

Oxygen Content

The maximum allowable oxygen content is currently 3.5 wt percent for ethanol blends. However, modern vehicles can generally perform adequately with oxygen levels of 5 to 6 wt percent. In the low petroleum cases, the maximum allowable oxygen content is 6 wt percent. Extrapolation assumptions are required for use of the Complex Model beyond its valid limit of 3.7 wt percent oxygen.

Energy Content

BTU content is not the sole determinant of fuel economy. Other characteristics of the fuel, as well as vehicle related factors, may also affect fuel economy. Although oxygenates contain less energy than some other gasoline components, their presence in gasoline chemically enleans the air/fuel charge, which can result in more complete combustion of fuel (DA 1992). The implied costs of per gallon fuel economy changes are included in the refining costs for low petroleum gasoline production.

Hydroprocessing may be very important in some low petroleum gasoline production cases, with possible side effects on the amounts of severely hydroprocessed stocks blended to distillates. Therefore, specifications have to be imposed on some distillate products to prevent problems with fuel stability and lubricity.

Economic Assumptions

The PADD III refiner price for crude oil is based on a long-run supply elasticity of 0.3 and a reference crude oil price of $26.49 per barrel (1990 U.S. dollars) for the year 2010 (DOE/EIA 1994a). The crude oil price is used to estimate prices for individual refined products, by applying price ratios and differentials that have remained nearly constant in recent decades (Obel 1986). Ether prices are based on National Petroleum Council estimates.

The PADD III refiner price for natural gas is based on a long-run supply elasticity of 0.3 and an average dry gas price of $3.17 per MCF (1990 U.S. dollars) for the year 2010 (DOE/EIA 1994a).

The PADD III refiner price for corn-derived ethanol is assumed to follow the supply curve in Fig. 1. The ethanol supply curves include the federal tax credit of 54 cents per gallon. The price of cellulosic ethanol is assumed to be the sum of (1) the feedstock cost from a nearly flat supply curve and (2) the cost of manufacturing conversion, with (3) the federal tax credit. In the low petroleum study, the cellulosic ethanol price faced by the refiner is in the range of $16.24 to $16.88 per barrel.

Low petroleum gasoline production can involve substantial substitution of natural gas for crude oil. Because of increased gas demand, the price of natural gas increases. With decreased demand for crude oil, the price of crude oil falls. Product prices are affected by a price reduction driven by the falling crude oil price, and a price increase due to the increased costs of natural gas and refining. The low petroleum study assumes that the demand for refined products is constant, regardless of the net price effect. In actual markets, the demand could change with changes in price.

Capital equipment investment is based on a 15 percent discounted cash flow rate of return on investment (ROI), with accounting for seasonal process utilization changes.

Refining costs (and fuel economy cost effects) are relative to year 2010 seasonal base cases with production of 100 percent CG. The Base cases (cost reference cases) use current refinery capacity plus additional (sunk cost) investment capacity (DOE/EIA 1994b).

Low Petroleum Gasoline Components

EPACT defines replacement fuel as "the portion of any motor fuel that is methanol, ethanol, or other alcohols, natural gas, liquefied petroleum gas, hydrogen, coal derived liquid fuels, fuels (other than alcohol) derived from biological materials, electricity (including electricity from solar energy), ethers, or any other fuel the Secretary [of Energy] determines, by rule, is substantially not petroleum and would yield substantial energy security benefits and substantial environmental benefits." For the study of low petroleum gasoline production, this means that replacement fuels can include portions of gasoline meeting the above definition whether by direct blending or by conversion into other components.

Methanol (derived from natural gas) and ethanol can be directly blended into gasoline for replacement fuel credit. Gasoline grade tertiary butyl alcohol (GTBA) is directly blended as a cosolvent with methanol. Methanol and ethanol can also be converted into ethers.

Replacement fuel credit is given for purchased methyl tertiary butyl ether (MTBE) and ethyl tertiary butyl ether (ETBE), which are assumed to be derived from non-petroleum sources. For ethers produced in the refinery itself, the associated alcohol is credited as a replacement fuel. Produced ethers can include MTBE, tertiary amyl methyl ether (TAME), tertiary hexyl methyl ether (THME), ETBE, tertiary amyl ethyl ether (TAEE), and tertiary hexyl ethyl ether (THEE).

Replacement fuel credit is also given for a portion of hydrogen derived from non-petroleum sources; and for purchased components of natural gas liquids (NGLs include ethane, propane, butanes and natural gasoline). NGL components may be used in the production of ethers, alkylate, reformate and other gasoline blendstocks. If large volumes of ethers are used in low petroleum gasoline, production costs could be particularly sensitive to the availability of NGL component raw materials for ether production.

Production of Low Petroleum Gasoline

The twenty-three cases of the low petroleum study examine the effects of hypothetical low petroleum gasoline formulations on PADD III refinery operations and costs (Hadder 1995). The study cases are not forecasts of low petroleum gasolines that will enter the marketplace. Rather, the cases provide an assessment of future refinery capability, and case study results suggest that the 30 percent replacement fuel target can be achieved with gasoline-based fuels alone, albeit at a high cost. Compared to the Base case, incremental costs to meet the 30 percent low petroleum target could be more than three times the incremental costs to produce Phase II reformulated gasoline in PADD III. High oxygenation is the key to meeting the replacement fuel target, and major contributors to cost increase can include investment in processes to produce and etherify light olefins. High oxygenation can also increase the costs of control of RVP, distillation properties, and pollutant emissions of gasolines. Crude oil reduction, with decreased dependence on foreign sources, is a major objective of the low petroleum program. In the analysis, total crude oil used by the modeled refinery is reduced by 10 to 17 percent.

Compared with summer gasolines, emissions constraints are less stringent for winter gasolines, and production costs are lower. If the winter gasoline production season is 6.5 months, then year-round low petroleum gasoline with near-30 percent non-petroleum components might be achieved by combinations of cases, including:

Methyl Ether Cases

Fig. 2 shows a summer-winter combination for methyl ethers that has an annualized refining cost increase of 37 cents per gallon of gasoline and a non-petroleum share of 29 percent. Crude oil used by the refinery is reduced by 10 percent, at an annualized cost of $89 per barrel (Fig. 3). Compared to base case gasolines, this summer-winter combination reduces GHG emissions by 0.5 percent (Fig. 4) and satisfy the minimum requirements for reduction of other pollutant emissions.

Tables 2 and 3 summarize the use of low petroleum components and process investment for seasonal cases with use of methyl and ethyl ethers. The summer methyl ether case is characterized by increased utilization of molecule building processes such as polymerization and dimerization. In the methyl ether winter case, C4s are need to build blendstocks (heavier alkylate and polymer gasoline) for control of distillation properties.

Ethyl Ether Cases

Fig. 2 shows a summer-winter combination for ethyl ethers that has an annualized refining cost increase of 23 to 33 cents per gallon of gasoline and a non-petroleum share of 34 percent. Crude oil use is reduced by 12 percent, at an annualized cost of $48 to $68 per barrel (Fig. 3). The lower costs are for use of cellulosic ethanol, and the higher costs are for use of corn-derived ethanol. The summer-winter combination based on corn-derived ethanol increases GHG emissions by 2.8 percent, compared to base case gasolines (Fig. 4). However, the combination based on cellulosic ethanol decreases GHG emissions by 15.9 percent, compared to base case gasolines.

In the ethyl ether summer cases of Tables 2 and 3, increased natural gas feedstocks are used in expanded hydrogen plant capacity. The increased hydrogen stream is utilized in expanded hydrocracker capacity, with increased volumes of hydrocracked stocks blended to gasolines and distillates. There is substantial investment in ether plant and light olefins production for etherification. The high percentage of ETBE is related to high levels of automotive acetaldehyde emissions. The Complex Model for emissions has been used beyond the valid limit for oxygen content in gasoline, with a greater-than-linear increase in acetaldehyde emissions. If the acetaldehyde emissions is assumed to be linear, then refining costs are reduced by a substantial 10 to 12 cents per gallon in the ethyl ether summer case.

The ethyl ether winter case requires less distillation correction than the methyl ether case. C4 availability is greater, and cost is lower for ether production.

For the year-round cases, a refiner would not choose to produce low petroleum gasoline unless the average cost of crude in the base case is somewhere in the range of costs to reduce crude oil use: $48 to $89 per barrel. A mix of strategies could be less costly than any of the cases examined in this study. For example, costs might be lower with production of regional mixes of ether-based and ethanol-based gasolines in the winter, and with mixes of ether-based gasolines in the summer.

Conclusion

Analysis of year 2010 production of low petroleum gasoline suggests that the 30 percent replacement fuel target is achievable without introducing alternative-fueled vehicles. However, incremental costs for production of low petroleum gasoline could be more than three times the incremental costs to produce Phase II RFG in the U.S. Gulf Coast refining region. Given the increasing cost of production of low petroleum gasolines, as higher levels of substitution are achieved, introducing alternative-fueled vehicles at some point, perhaps between the 10 percent and 20 percent replacement fuel level, may be a better route to reduce reliance on petroleum-based fuels, even with the infrastructure investments needed for alternative fuels.

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Table 2. PADD III Low Petroleum Components for Year 2010

Case:	Methyl ethers		Ethyl ethers	
	Summer	Winter	Summer	Winter
RFG oxygen target, wt%	6.0	6.0	6.0	6.0
CG oxygen target, wt%	6.0	6.0	6.0	6.0
Crude reduction target, vol%	10	10	17.0	10
Oxygenate imports allowed, vol%	71	66	43	70
Components:				
Crude, MBD	5521	5187	5072	5015
Crude reduction, vol%	10.0	10.0	17.3	13.0
Hydrogen from natural gas, MBD (GE)[a]	0	0	81.0	15.4
Natural gasoline, MBD (GE)		65.4	96.1	90.9
Ethane, MBD (GE)	2.8	3.4	2.8	
Propane, MBD (GE)	6.4	5.1		
Butanes, MBD (GE)	171.2	174.2	176.5	159.7
Methanol from natural gas, MBD (GE)	54.2	56.3		
MTBE imported, MBD (GE)	694.7	568.2		
Ethanol, MBD (GE)			220.3	100.7
ETBE purchased, MBD (GE)			490.1	708.0
Total non-petroleum, MBD (GE)	929.3	876.1	1066.7	1074.7
Non-petroleum share, allocated to gasoline, %	27.7	29.6	31.8	36.5

[a]GE is gasoline energy equivalent

Table 3. PADD III Process Capacity Investments for Year 2010

Case:	Methyl ethers	Ethyl ethers		
	Summer	Winter	Summer	Winter
RFG oxygen target, wt%	6.0	6.0	6.0	6.0
CG oxygen target, wt%	6.0	6.0	6.0	6.0
Crude reduction target, vol%	10	10	10	10
Oxygenate imports allowed, vol%	71	66	43	70
Process capacity investments, MBD:	15 percent ROI			
FCC feed hydrofiner	513	272		
FCC gasoline fractionation	927	969	955	71
Polymerization	585	289	44	
Butane isomerization			221	
Butylene isomerization	15			
C5/C6 isomerization	32			
Resid desulfurizer	432	85		
Resid cracker		4		
Thermal cracker (gas feed)	508	71		
Cryogenic fractionation	312	234		
Dimerization (of ethylene)	223	193		
Gas oil hydrocracker	105		203	
C2-C5 dehydrogenation	29	78	410	
Ether plant			702	
Hydrogen production (MMSCFD)	1611		1354	248
Naphtha cracker	594	318	788	358
Distillate deep hydrotreater	77			
Sulfur plant, M tons per day	0.8			
Coker (fluid)	260			
Reformer	72			
Reformate splitter	13		522	
Hydrogenation of C5/C6 olefins	156	22		
LPG aromatization	152		7	105
Aromatics recovery	10			
Investment cost ($MM)	37,900	16,200	36,800	4,200