ปฏิกิริยาอีเทอริฟิเคชันของแก๊สโซลีนจากกระบวนการฟลูอิไดซ์คะตะไลติกแครกกิงกับกลีเซอรอล

นางสาวศิริมา สุวรรณมณี

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ETHERIFICATION OF GASOLINE FROM FLUIDIZED CATALYTIC CRACKING WITH GLYCEROL

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ศิริมา สุวรรณมณี: ปฏิกิริยาอีเทอริฟิเคชันของแก๊สโซลีนจากกระบวนการฟลูอิไดซ์คะตะไลติกแครกกิงกับกลีเซอรอล (ETHERIFICATION OF GASOLINE FROM FLUIDIZED CATALYTIC CRACKING WITH GLYCEROL) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: ศ. ดร. สุทธิชัย อัสสะบำรุงรัตน์, อ. ที่ปรึกษาวิทยานิพนธ์ร่วม: ผศ. ดร. วรพล เกียรติกิตติพงษ์, 183 หน้า

งานวิจัยนี้ศึกษาปฏิกิริยาการเกิดอีเทอร์ระหว่างแก๊สโซลีนจากกระบวนการฟลูอิไดซ์คะตะไลติกแครกกิงกับกลีเซอรอลโดยทำการทดลองและการสร้างแบบจำลอง จากกระบวนการฟลูอิไดซ์คะตะไลติกแครกกิงมีโอลีฟินส์ที่ว่องไวสำหรับผลิตสารประกอบอีเทอร์อยู่มาก และในทางกลับกันสารประกอบโอลีฟินส์ ซึ่งสารที่เกิดขึ้นใหม่นั้นค่าความเข้มข้นจะต้องลดปริมาณลงให้ไม่เกิน 18 % ตามข้อกำหนดมาตรฐานยูโร 4 เป็นตัวเพิ่มปริมาณเชื้อเพลิงไปพร้อมกันปฏิกิริยาที่เกิดขึ้นนั้นเป็นการปรับปรุงคุณภาพของแก๊สโซลีนโดยใช้กลีเซอรอลเป็นตัวเข้าทำปฏิกิริยาด้วย เมื่อนำน้ำมันที่ได้จากปฏิกิริยาการเกิดอีเทอร์ของแก๊สโซลีนมาวิเคราะห์พบว่าให้ค่าออกเทนสูงขึ้นและค่าความดันไอของสารผสมมีค่าต่ำลงเมื่อเทียบกับแก๊สโซลีตั้งต้นเป็นไปตามที่ต้องการ และจากการศึกษาพบว่าสภาวะที่เหมาะสมสำหรับปฏิกิริยานี้คือการป้อนเข้าของแก๊สโซลีนต่อกลีเซอรอลในอัตราส่วน 4:1 ที่อุณหภูมิ 70° C และใช้ตัวเร่งปฏิกิริยาคือแอมเบอร์ลิส 16 ปริมาณ 10 กรัม โดยเวลาในการดำเนินของปฏิกิริยาคือ 10 ชั่วโมง สำหรับการศึกษาสมดุลทางเทอร์โมไดนามิกส์ของปฏิกิริยาการเกิดอีเทอร์ระหว่างแก๊สโซลีนจากกระบวนการฟลูอิไดซ์คะตะไลติกแครกกิงกับเอทานอลโดยใช้โปรแกรมจำลองแอสเพนพลัส เวอร์ชัน 11.1 องค์ประกอบของแก๊สโซลีนจะมีอะตอมคาร์บอนอยู่ในช่วง 4-7 อะตอม วิธีการประมาณค่าคุณสมบัติของสาร (เช่น วิธีของโจแบค วิธีของกานี วิธีของเบนสัน) ได้ถูกนำมาใช้เพื่อประมาณค่าคุณสมบัติต่างๆ ที่ไม่สามารถหาได้ (เช่น ความดันวิกฤต อุณหภูมิวิกฤต จุดเดือด และค่าพลังงานอิสระการก่อเกิดสารที่สภาวะมาตรฐาน) จากการเลือกขั้นต้นพบว่าวิธีของโจแบคสามารถทำนาย ค่าอุณหภูมิวกฤต, ค่าความดันวิกฤต, จุดเดือด และค่าพลังงานอิสระการก่อเกิดสารที่สภาวะมาตรฐาน ได้เป็นอย่างดี อย่างไรก็ตาม การใช้วิธีการกรุ๊ปคอนทริบูชันเพื่อหาค่าการเปลี่ยนไปขององค์ประกอบนั้นพบว่ามีเพียงกลีเซอรอลและ คาร์บอน 4 อะตอมของโอลีฟินส์เท่านั้นที่สอดคล้องกับการทดลอง ในขณะที่ค่าคอนเวอร์ชันของคาร์บอน 5 อะตอมและคาร์บอน 6 อะตอมของโอลีฟินส์นั้นมีค่าที่ไม่ใกล้เคียงกับการทดลอง

ภาควิชา วิศวกรรมเคมี
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ลายมือชื่อนิสิต ศิริมา สุวรรณมณี
ลายมือชื่ออ.ที่ปรึกษาวิทยานิพนธ์หลัก
ลายมือชื่ออ.ที่ปรึกษาวิทยานิพนธ์ร่วม

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KEYWORDS: FCC GASOLINE/ GLYCEROL/ ETHERIFICATION/ SIMULATION

SIRIMA SUWANMANEE: ETHERIFICATION OF GASOLINE FROM FLUIDIZED CATALYTIC CRACKING WITH GLYCEROL. ADVISOR: PROF. SUTTICHAI ASSABUMRUNGRAT, Ph.D., CO-ADVISOR: ASST. PROF. WORAPON KIATKITTIPONG, D.Eng, 183 pp.

This thesis investigates etherification reactions between gasoline from fluidized catalytic cracking (FCC) and glycerol both experimental and thermodynamic modeling. FCC gasoline is a potential valuable feedstock of reactive olefins for production of oxygenated ethers. On the contrary, these olefinic compounds should be diminished also in order to meet the new mandatory of gasoline composition which allows the olefin content not to exceed 18 vol% as regulated by Euro 4 standard. The reaction showed a promising process for gasoline quality improvement and utilization of glycerol as a fuel extender simultaneously. The etherified FCC gasoline showed higher research octane number (RON) and lower blending Reid vapor pressure (bRvp) which are preference properties. The suitable operating condition of reaction were carried out by feeding FCC to glycerol ratio of 4:1 with operating temperature of 70 °C, 10 g of Amberlyst 16 catalyst and 10 hours of reaction time. The thermodynamic modeling was investigated by using a simulation program, Aspen plus version 11.1. The components of gasoline consist of carbon atom ranging from C4-C7. The group contribution methods (i.e. Joback's method, Gani's method and Benson's method) were applied to estimate the missing parameters (e.g. critical pressure, critical temperature, boiling point, stardard Gibb's free energy of formation). The preliminary selection of group contribution method shows that Gani's and Joback's method are well-predicted for normal boiling point, critical temperature and critical pressure and standard Gibb's free energy of formation. However, using the group contribution method to estimate conversion give good agreement for only glycerol and C4 olefin while C5-C6 olefins conversion are quite far from the experimental results.

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Field of Study: Chemical Engineering....... Advisor's Signature ....
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NOMENCLATURE

T_c	critical temperature	[K]
P_c	critical pressure	[atm]
T_b	normal boiling point	[K]
$\Delta H_f^o(298.15K)$	standard enthalpy of formation	[kJ/mol]
$C_p^o(T)$	heat capacity	[J/mol K]
$S_f^o(298.15)$	standard entropy of formation	[J/mol K]
$\Delta G_f^o(298.15)$	standard Gibbs free energy of formation	[kJ/mol]
S_s^s	entropy of symmetry	[J/ mol K]
S_{el}	entropy of the elements	[J/mol K]

Subscripts

approx	approximately
Δ_T	sum contributions for various atom for temperature
Δ_P	sum contributions for various atom for pressure
N_k	number of First-order groups of type k in the molecule
tbk	normal boiling point of subgroup k
tb1k	normal boiling point of first order subgroup k
tb2j	normal boiling point of second order subgroup j
tck	critical temperature of subgroup k
tc1k	critical temperature of first order subgroup k
tc2j	critical temperature of second order subgroup j
pck	critical pressure of subgroup k
pc1k	critical pressure of first order subgroup k
pc2j	critical pressure of second order subgroup j
gfk	gibbs free energy of formation of subgroup k
gf1k	gibbs free energy of formation of first order subgroup k
gf2j	gibbs free energy of formation of second order subgroup j
N_{atoms}	number of atom in molecule
M	molecular structure

f	linear or nonlinear function
F_{1j}	contribution for the First-Order group
F_{2j}	contribution for the second-order group
M_j	number of second-order groups of type j in the molecule
N_{oi}	number of structural isomers of the molecule
N_{ts}	total symmetry number
N_{is}	number of internal symmetry
N_{es}	number of external symmetry
G^E	excess Gibbs free energy
x_i	fraction of components i
θ_i	area fraction
ϕ_i	volume fraction
r_i	relative volume
q_i	relative surface area
γ_I	activity coefficient of component i
γ^C	combination activity coefficient
γ^R	residual activity coefficient
$v_k^{(i)}$	number of subgroups of type k in a molecule of species i
R_k, Q_k	values of the subgroup parameters
a_{mk}	group interaction parameters

Abbreviations

FCC	Fluidize Catalytic Cracking
MTBE	Methyl tert-butyl ether
TAME	Tert-amyl methyl ether
CO	Carbon monoxide
CO_2	Carbon dioxide
NOx	Nitrogen oxide [NO, NO_2]
THEE	Tert-hexyl ethyl ether
ETBE	Ethyl tert-butyl ether
TAEE	Tert-amyl ethyl ether
DIPE	Diisopropyl ether
LPG	Liquid petroleum gas

Rvp	Reid vapor pressure
ASTM	American Society for Testing and Materials
MON	motor octane number
RON	research octane number
FBP	Final boiling point
IBP	Initial boiling point
EPA	Environmental Protection Agency
2M1B	2-methyl-1-butene
2M2B	2-methyl-2-butene
DVB	divinylbenzene
bRvp	blending Reid vapor pressure
IB	isobutene
IA	isoamylene
CSTR	continuous stirred tank reactor
DI	Driveability index
H_2O	water
SBU's	secondary building units
TAA	tert-amyl ethyl ether
TBA	tert-butyl alcohol
VOCs	volatile organic compounds
2M1P	2-methyl-1-pentene
2M2P	2-methyl-2-pentene
C3M2P	cis-3-methyl-2-pentene
23DM1B	2,3-dimethyl-1-butene
MCYP	1-methylcyclopentene
C3M2H	cis-methyl-2-hexene
C3M3H	cis-3-methyl-3-hexene
T3M3H	trans-3-methyl-3-hexene
2E1P	2-ethyl-1-pentene
23DM2P	2, 3-dimethyl-2-pentene
C34DM2P	cis-3,4-dimethyl-2-pentene
2E3M1B	2-ethyl-3-methyl-1-butene
24DM1P	2, 4-dimethyl-1-pentene
3E2P	3-ethyl-2-pentene

T2M3H	Tran-2-methyl-3-hexene
MOTMH1	3-(1-ethyl-3-methyl butoxy)-1,2-propanediol
MOTMH2	2-(1-ethyl-3-methyl butoxy)-1,3-propanediol
DITMH1	1,3-bis(1-ethyl-3-methyl butoxy)-2-propanol
DITMH2	2,3-bis(1-ethyl-3-methyl butoxy)-1-propanol
TRITMH	1,2,3-tris-(1-ethyl-3-methyl butoxy)- propane
33D	3,3-dimethyl-1-pentene
MO33D1	3-(1,1-dimethyl pentoxy)-1,2-propanediol
MO33D2	2-(1,1-dimethyl pentoxy)-1,3-propanediol
DI33D1	1,3-bis(1,1-dimethyl pentoxy)-2-propanol
DI33D2	2,3-bis(1,1-dimethyl pentoxy)-1-propanol
TRI33D	1,2,3-tris-(1,1-dimethyl pentoxy)- propane
3MET-02	3-methyl-1-pentene
MO3M1	3- (3-ethyl -pentoxy)-1,2- propanediol
MO3M2	2 -(3-ethyl -pentoxy)-1,3- propanediol
DI3M1	1,3-bis(3-ethyl-pentoxy)-2-propanol
DI3M2	2,3-bis(3-ethyl- pentoxy)-1-propanol
TRI3M	1,2,3-tris-(3-ethyl- pentoxy)- propane
4MET-02	Cis-4-methyl-2-pentene
4MET-01	4-methyl-1-pentene
MO4ME1	3 -(1,4-dimethyl -butoxy)-1,2- propanediol
MO4ME2	2 -(1,4-dimethyl -butoxy)-1,3- propanediol
DI4ME1	1,3-bis(1,4-dimethyl- butoxy)-2-propanol
DI4ME2	2,3-bis(1,4-dimethyl- butoxy)-1-propanol
TRI4ME	1,2,3-tris-(1,4-dimethyl-butoxy)- propane
3ETH-01	3-ethyl-1-pentene
MOETH1	3-(1-methyl-2-ethyl-butoxy)-1,2-propanediol
MOETH2	2-(1-methyl-2-ethyl-butoxy)-1,3-propanediol
DIETH1	1,3-bis(1-methyl-2-ethyl-butoxy)-2-propanol
DIETH2	2,3-bis(1-methyl-2-ethyl-butoxy)-1-propanol
TRIETH	1,2,3-tris-(1-methyl-2-ethyl-butoxy)- propane
CMH	Cis-5-methyl-2-hexene
MOCMH1	3-(1,3-dimethyl-pentoxy)-1,2-propanediol
MOCMH2	2-(1,3-dimethyl-pentoxy)-1,3-propanediol

DICMH1	1,3-bis(1,3-dimethyl-pentoxy)-2-propanol
DICMH2	2,3-bis(1,3-dimethyl-pentoxy)-1-propanol
TRICMH	1,2,3-tris-(1,3-dimethyl-pentoxy)- propane
4MET-03	4-methyl-1-hexene
MO4M1	3-(4-methyl-hexoxy)-1,2-propanediol
MO4M2	2-(4-methyl-hexoxy)-1,3-propanediol
DI4M1	1,3-bis(4-methyl-hexoxy)-2-propanol
DI4M2	2,3-bis(4-methyl-hexoxy)-1-propanol
TRI4M	1,2,3-tris-(4-methyl-hexoxy)- propane
MIB1	3-tert-butoxy -1,2-propanediol
MIB2	2-tert-butoxy -1,3-propanediol
DIB1	1,3-di-tert-butoxy-2-propanol
DIB2	2,3-di-tert-butoxy-1-propanol
TTIB	1,2,3- tri-tert-butoxy-propane
MMB1	3(1,1-dimethyl-propoxy)-1,2- propanediol
MMB2	2(1,1-dimethyl-propoxy)-1,3- propanediol
DMB1	1,3-bis-(1,1-dimethyl propoxy) -2-propanol
DMB2	2,3-bis-(1,1-dimethyl propoxy) -1-propanol
TMB	1,2,3-tris-(1,1-dimethyl propoxy)-propane
MMP1	3-(1,1-dimethyl butoxy)-1,2-propanediol
MMP2	2-(1,1-dimethyl butoxy)-1,3-propanediol
DMP1	1,3-bis (1,1-dimethyl butoxy)-2-propanol
DMP2	2,3-bis (1,1-dimethyl butoxy)-1-propanol
TMP	1,2,3-tris(1,1-dimethyl butoxy)-propane
MEB1	3-(1-methyl-2-ethyl-propoxy)-1,2-propanediol
MEB2	2-(1-methyl-2-ethyl-propoxy)-1,3-propanediol
DEB1	1,3-bis (1,1-methyl-2-ethyl- propoxy)-2- propanol
DEB2	2,3-bis (1,1-methyl-2-ethyl -propoxy)-1- propanol
TEB	1,2,3-tris (1-methyl-2-ethyl- propoxy)- propane
M23DB1	3-(1,1,2-trimethyl-propoxy)-1,2-propanediol
M23DB2	2-(1,1,2-trimethyl-propoxy)-1,3-propanediol
D23DB1	1,3-bis(1,1,2-trimethyl-propoxy)-2-propanol
D23DB2	2,3-bis(1,1,2-trimethyl-propoxy)-1-propanol
T23DB	1,2,3-tris(1,1,2-trimethyl-propoxy)-propane

MMCYP1	3-(1-methyl cyclopentyloxy)-1,2-propanediol
MMCYP2	2-(1-methyl cylopentyloxy)-1,3-propanediol
DMCYP1	1,3-bis-(1-methyl cyclopentyloxy)-2-propanol
DMCYP2	2,3-bis-(1-methyl cyclopentyloxy)-1-propanol
TMCYP	1,2,3-tris(1-methyl cylopentyloxy)-propane
MEP1	3-(1,1-diethyl propoxy)-1,2-propanediol
MEP2	2-(1,1-diethyl propoxy)-1,3-propanediol
DEP1	1,3-bis(1,1-diethyl propoxy)-2-propanol
DEP2	2,3-bis(1,1-diethyl propoxy)-1-propanol
TEP	1,2,3-tris(1,1-diethyl propoxy)-propane
M2EP1	3-(1-methyl-1-ethyl-butoxy)-1,2-propanediol
M2EP2	2-(1-methyl-1-ethyl-butoxy)-1,3-propanediol
D2EP1	1,3-bis(1-methyl-1-ethyl-butoxy)-2-propanol
D2EP2	2,3-bis(1-methyl-1-ethyl-butoxy)-1-propanol
T2EP	1,2,3-tris(1-methyl-1-ethyl-butoxy)- propane
M23DP1	3-(1,1,2-trimethyl-butoxy)-1,2-propanediol
M23DP2	2-(1,1,2-trimethyl-butoxy)-1,3-propanediol
D23DP1	1,3-bis(1,1,2-trimethyl-butoxy)-2-propanol
D23DP2	2,3-bis(1,1,2-trimethyl-butoxy)-1-propanol
T23DP	1,2,3-tris(1,1,2-trimethyl-butoxy)- propane
MEMP1	3-(1-methyl-1-isopropyl propoxy)-1,2-propanediol
MEMP2	2-(1-methyl-1-isopropyl propoxy)-1,3-propanediol
DEMP1	1,3-bis(1-methyl-1-isopropyl propoxy)-2-propanol
DEMP2	2,3-bis(1-methyl-1-isopropyl propoxy)-1-propanol
TEMP	1,2,3-tris(1-methyl-1-isopropyl propoxy)-propane
M24DP1	3-(1,1,3-tris methyl butoxy)-1,2-propanediol
M24DP2	2-(1,1,3-tris methyl butoxy)-1,3-propanediol
D24DP1	1,3-bis(1,1,3-tris methyl butoxy)-2-propanol
D24DP2	2,3-bis(1,1,3-tris methyl butoxy)-1-propanol
T24DP	1,2,3-tris(1,1,3-tris methyl butoxy)- propane

CHAPTER I

INTRODUCTION

Rational

Nowadays global warming and energy crisis are recognized as the most global severe problems. The transportation might be a significant part of the concern. Biodiesel is an alternative fuel that is produced by chemically reacting a vegetable oil or animal fat with an alcohol such as methanol or ethanol. An advantage of biodiesel is that it is "carbon neutral" in terms of CO_2 since the CO_2 has recently come from the atmosphere through fixation by planting. However, for every 9 kg of biodiesel produced, about 1 kg of a crude glycerol by-product is formed (Dasari et al., 2005). As the biodiesel production is increasing exponentially, the crude glycerol generated from the transesterification has also been generated in a large quantity carrying thus an oversupply (Karinen et al., 2006). Glycerol can be utilized in personal care and cosmetics industrial and is a raw material to produce syn gas (H_2 + CO) or others hydrocarbons using processes such as pyrolysis, steam gasification and catalytic reforming reaction (Chaudhari et al., 2002)

Etherification of glycerol is one of promising processes for oxygenate fuel production. Isobutylene reacts with glycerol of acid catalyst and a mixture of mono-, di- and tri-tert-butyl ethers of glycerol is formed. Higher glycerol ether mainly di- and tri-tert-butyl ethers could be similar as the current commercial oxygenate additive used as oxygenates to gasoline and suggest an alternative to oxygenates such as methyl-tert-butyl ether (MTBE) and ethyltert- butyl ether (ETBE), which are presently used in fuel (Karinen et al., 2006). Addition of these ethers has positive effect on the quality of gasoline and preferentially ethers are active by reduction of fumes and particulate matters, carbon oxides and carbonyl compounds in exhaust. These ethers can reduce the emissions, mainly particulate matters, carbon oxide, and carbonyl compounds in exhaust gases (Kesling et al., 1994 and Girolamo et al., 1997). Moreover, glycerol ether oxygenates can decrease the cloud point (CP) of diesel fuel when combined with biodiesel (Noureddini et al., 2000). Although, glycerol ethers are mainly studied as diesel fuel additives, high octane numbers for the mixture of ethers in gasoline has been reported (112–128 (BRON) and 91– 99 (BMON)) (Wessendorf et al., 1995). However, until now the research works are limited with only two etherification agents isobutylene (IB) and tert-butyl alcohol (TBA) for the etherification with glycerol (Noureddini et al., 1998), (Klepacova et al., 2005; Klepacova et al., 2006),(Karinen et al., 2006).

FCC gasoline contained many C_4-C_8 reactive olefins e.g. IB, isoamylene (IA) which is a promising source for etherification. On the contrary, these olefins content should be eliminated or minimized before using as a gasoline in the environment viewpoint. The etherification of entire FCC gasoline have been successful experimented with methanol (Pescarollo et al., 1993) and ethanol (Kiatkittipong et al., 2008, 2009). Kiatkittipong et al., 2008 studied etherification of FCC gasoline with ethanol catalyzed by commercial catalysts, i.e., Amberlyst 16 and β-zeolite. Comparing between two catalysts, β-zeolite was a more suitable catalyst for the etherification of FCC gasoline with ethanol because not only a better catalytic activity for etherification, but some isomerization also occurs without aromatization. It offered products with higher RON and ethanol conversion with lower bRvp. A satisfied drivability index showed the cold start problem might not be occurred even in low bRvp (Kiatkittipong et al., 2009).

In this study, the process was investigated by etherifying the entire FCC gasoline with glycerol catalyzed by commercial catalyst. The suitable operating conditions (temperature, amount of catalysts) were primarily screened. The properties of etherified gasoline product, i.e., RON, bRvp and distillation temperature were compared with original FCC gasoline. Apart from the experimental section, thermodynamic analysis was also considered in this study. Since many components in the system are usually lack of thermodynamic properties, several group contribution methods were employed and compared with available properties of some chemical species. The results from the experiment and thermodynamic equilibrium estimation were preliminary compared and discussed.

CHAPTER II

THEORY

This chapter contributes some background information necessary for of the fuel oil quality improvement by the etherification of FCC gasoline with glycerol and etherification of glycerol. Some detail gasoline properties (octane number, bRvp and distillation temperature), oxygenates compound, FCC gasoline and catalysts (ion exchange resin and Beta-zeolite) were provided.

2.1 Fluidized Catalytic Cracking (FCC)

Fluidize catalytic cracking, developed by American engineers Warren K. Lewis and Edwin R. Gilliland, is a commonly used process and a modern oil refinery will typically include a cat cracker, particularly at refineries in the USA due to the high demand for gasoline. The process was first used in around 1942, and employs a powdered catalyst. During the Second World War, it provided Allied Forces with plentiful supplies of gasoline and artificial rubber that contrasted with the penury suffered by the Axis Forces. Initial process implementations were based on a low activity alumina catalyst and a reactor where the catalyst particles were suspended in a rising flow of feed hydrocarbons in a fluidized bed. Alumina-catalyzed cracking systems are still in use in high school and university laboratories in experiments concerning alkanes and alkenes. The catalyst is usually obtained by crushing pumice stones, which contain mainly aluminum oxide and silicon (IV) oxide into small, porous pieces. In the laboratory, Aluminum oxide (or porous pot) must be heated. In newer designs, cracking takes place using a very active zeolite-based catalyst in a short-contact time vertical or upward sloped pipe called the "riser". Pre-heated feed is sprayed into the base of the riser via feed nozzles where it contacts extremely hot fluidized catalyst at 1230 to 1400 °F (665 to 760 °C). The hot catalyst vaporizes the feed and catalyzes the cracking reactions that break down the high molecular weight oil into lighter components including LPG, gasoline, and diesel. The catalyst-hydrocarbon mixture flows upward through the riser for just a few seconds and then the mixture is separated via cyclones. The catalyst-free hydrocarbons are routed to main fractionators for separation into fuel gas, LPG, gasoline, light cycle oils used in diesel and jet fuel, and heavy fuel oil. During the trip up the riser, the cracking catalyst is "spent" by reactions which deposit coke on the catalyst and greatly reduce activity and selectivity. The "spent" catalyst is disengaged from the cracked hydrocarbon vapors and sent to a stripper where it is contacted with steam to remove hydrocarbons remaining in the catalyst pores. The "spent" catalyst then flows into a fluidized-bed regenerator where air (or in some cases air plus oxygen) is used to burn off the coke to restore catalyst activity and also provide the necessary heat for the next reaction cycle, cracking being an endothermic reaction. The "regenerated" catalyst then flows to the base of the riser, repeating the cycle. The gasoline produced in the FCC unit has an elevated octane rating but is less chemically stable compared to other gasoline components due to its olefinic profile. Olefins in gasoline are responsible for the formation of polymeric deposits in storage tanks, fuel ducts and injectors.

The FCC process continues to play an important role as gasoline producing unit in most oil refineries. FCC processes and catalysts are object to being developed to maximize the production of light olefins for petrochemical usage while maintaining high gasoline yield (Jakkula et al., 1998, Chan et al., 1999 and Corma et al., 1996).

Table2.1. Fluidized bed catalytic cracking adjusted for maximum production of middle distillates typical yield (Chauvel, A. and Lefebvre, G et al., 1989).

Products	% Weight of feedstock
C_{2-}	4.4
C_3 cut	2.7
C_4 cut	4.9
C_5 cut	5.0
Gasoline	27.5
Light gas oil	43.0
Residue (heavy fuel oil)	8.5
Coke (burned in the unit)	4.0
Total	100.0

2.2 Fuel oil properties

The worldwide has aware of the limitations of energy supplies. Alternative energy sources must meet certain criteria to be competitive with conventional fuels. Some of the special requirements these energy supplies will have to meet are as follows;

1. Fuels must be capable of being stored over extend time periods.

2. Storage, transportation and distribution of fuels used should be economical.

3. Handling of alternate fuels should not involve additional hazards such as fire, explosion, etc., in comparison to conventional fuels.

4. Alternate fuels should not impose major engineer changes to process and/or system using them.

Other traditional requirements were brief as follows.

2.2.1 Octane Number

Octane number, figure of merit representing the resistance of gasoline to premature detonation when exposed to heat and pressure in the combustion chamber of an internal-combustion engine. Such detonation is wasteful of the energy in the fuel and potentially damaging to the engine; premature detonation is indicated by knocking or pinging noises that occur as the engine operates. If an engine running on a particular gasoline makes such noises, they can be lessened or eliminated by using a gasoline with a higher octane number. The octane number of a sample of fuel is determined by burning the gasoline in an engine under controlled conditions, e.g., of spark timing, compression, engine speed, and load, until a standard level of knock occurs. The engine is next operated on a fuel blended from a form of isooctane that is very resistant to knocking and a form of heptane that knocks very easily. When a blend is found that duplicates the knocking intensity of the sample under test, the percentage of isooctane by volume in the blended sample is taken as the octane number of the fuel. Octane numbers higher than 100 are found by measuring the amount of tetraethyl lead that must be added to pure isooctane to duplicate the knocking of a sample fuel. At present three systems of octane rating are used in the United States. Two of these, the research octane (RON) and motor octane numbers (MON), are determined by burning the gasoline in an engine under different, but specified, conditions. Usually the motor octane number is lower than the research octane. The third octane rating, which federal regulations require on commercial gasoline pumps, is an average of research octane and motor octane. Under this system a regular grade gasoline has an octane number of about 87 and a premium grade of about 93.

A high tendency to autoignite, or low octane rating, is undesirable in a gasoline engine but desirable in a diesel engine. The standard for the combustion quality of diesel fuel is the cetane number. A diesel fuel with a high cetane number has a high tendency to autoignite, as is preferred.

Table2.2 The blending octane number of the oxygenates in typical gasoline (Thipsunet, 2006)

Oxygenates	Blending Octane Number		
	RON	MON	(RON+MON)/2
Ethers			
Methyl tertiary-butyl ether (MTBE)	117	101	110
Ethyl tertiary-butyl ether (ETBE)	118	101	111
Tertiary-amyl methyl ether (TAME)	112	98	105
Tertiary-amyl ethyl ether (TAEE)	105	95	100
Ethers of glycerol			
1- mono-tert-butyl ether of glycerol	112-128	91-99	
2-mono-tert-butyl ether of glycerol			
1,3-di-tert-butyl ether of glycerol			
1,2-di-tert-butyl ether of glycerol			
tri-tert-butyl ether of glycerol			
Alcohols			
Methanol	123	91	107
Ethanol	123	96	109.5
Tertiary-butyl alcohol (TBA)	106	89	97.5
Glycerol	-	-	-

2.2.2 Reid Vapor Pressure (Rvp)

Vapor pressure is an important physical property of volatile liquids. It is the pressure that a vapor exerts on its surroundings. Its units are kilopascals, corrected to one atmosphere (101.3 kPa). For volatile petroleum products, vapor pressure is used as an indirect measure of evaporation rate. Vapor pressure can be measured by a variety of methods including Reid, dynamic, static, isoteniscopic, vapor pressure balance, and gas saturation. The most commonly used method for crude oils was the Rvp, as determined by ASTM method D 323 - Standard Test Method for Vapor Pressure of Petroleum Products (Reid Method), (ASTM, 1996a). This test method determines vapor pressure at 37.8 ^{o}C (100 ^{o}F) of petroleum products and crude oils with initial boiling point above 0 ^{o}C (32 ^{o}F). It is measured by saturating a known volume of oil in an air chamber of known volume and measuring the equilibrium pressure which is then corrected to one atmosphere (101.3 kPa).

2.2.3 Distillation Temperature

Gasoline is a mixture of many different compounds, each having its own boiling point and vapor-forming characteristics. Thus gasolines show a boiling range covering a temperature spread of around 170^{o}C from the initial boiling point (IBP) to the final boiling point (FBP). The temperature range over which the gasoline distills will depend on the composition of the gasoline and the efficiency of the distillation column. A very efficiency column may be able to separate individual compounds if they have moderate differences in boiling point and if each is present a reasonable amount. Gasolines usually contain many readily identifiable compounds (up to about 400) that the distillation curve is quite smooth, even when a high degree of fractionation is used.

Figure 2.1 shows gasoline distillation curves obtained at two different levels of fractionation efficiency; curve A is the sort of curve that one might obtain with good fractionation, whereas curve B is the same gasoline but with very little fractionation using the standard ASTM D 86 test.It will be seen that the temperature at which the mixture begins to distill is much lower with a high degree of fractionation, and the final temperature is much higher, showing that individual compounds or groups of similar boiling compounds are separated much more readily in this case. If one wanted an even better separation, then techniques such as gas/liquid chromatography could be used.

The distillation curve can be observed that gasoline more volatile, one set of problems can occur, and if one goes too far in the other direction, another set of difficulties is possible. Weather conditions, particularly ambient temperature, influence the choice of volatility required for satisfactory operation. Altitude also has a small effect because atmospheric pressure affects the rate of evaporation of gasoline. Vehicles themselves vary enormously in the way that they respond to gasoline volatility is not closely matched to the weather conditions prevailing. The vehicle design aspect which is the most important in this respect is the proximity of the fuel system to hot engine parts. It is necessary to avoid excessive vaporization during hot weather and yet to make sure that there is enough heat present during cold weather to adequately vaporize the gasoline. Distillation data are often represented and specified by the temperature at which a given percentage of the gasoline is evaporated such as T10 is the temperature at which 10% volume of the gasoline is evaporated using ASTM D 86. Similarly, they can also be represented by the percentage evaporated at a given temperature so that E70 represents the percentage evaporated at 70^{o}C. It is considered preferable and more meaningful to use percentages evaporated rather than temperatures, particularly when carrying out blending calculations.

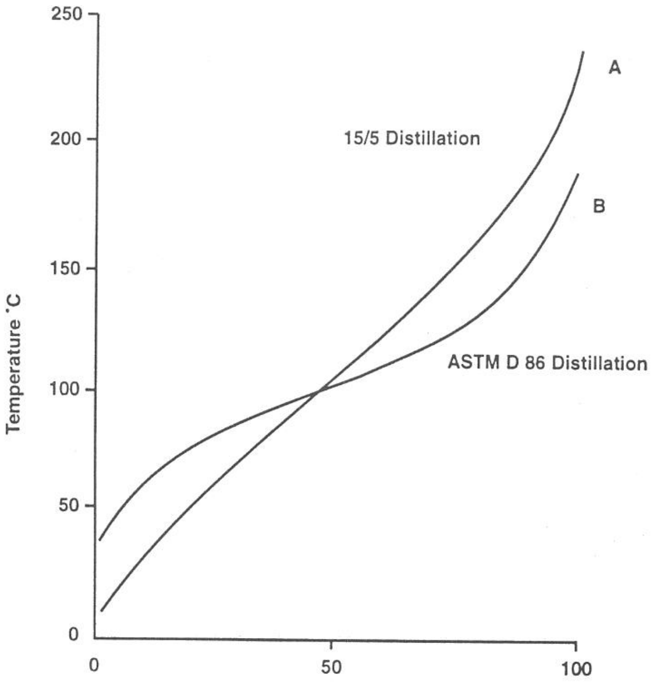


Figure 2.1 Gasoline distillation curve (Owen and Coley et al., 1995)

2.3 Glycerol

Glycerol is miscellaneous, utilizable product which is produced mainly from renewable source and glycerol forms as a by-product of transesterification reaction of natural oil with methanol. Such glycerol can be used due to its low price as initial raw material for many profitable products. But, the price depends on purity of obtained glycerol. Until recently, synthetic glycerol was mainly manufactured at an industrial scale from epichlorohydrin. Since glycerol forms the backbone of triglycerides, it is produced on saponification or transesterification. Soap-making and biodiesel production are respective examples. The reaction of isobutylene or other olefins with glycerol is one of possibilities of glycerol utilization. Isobutylene reacts with glycerol of acid catalyst and a mixture of mono-, di- and tri-tert-butyl ethers of glycerol is formed. Higher glycerol ether mainly di- and tri-tert-butyl ethers could be similar as the current commercial oxygenate additive used as oxygenates to gasoline. Furthermore, addition of these ethers has positive effect on the quality of gasoline and preferentially ethers are active by reduction of fumes and particulate matters, carbon oxides and carbonyl compounds in exhaust.

2.4 Etherification of glycerol

Glycerol ethers of interest include the compounds resulting from reaction with isobutylene or tert-butanol, including polyglycerols and glycosyl glycerol. Glycerol cannot be added directly to fuel since its high polarity makes it is virtually insoluble in conventional fuels (Mario et al., 2008). In addition, its hygroscopic properties make it unsuitable as a fuel additive in unmodified form. Moreover, glycerol polymerizes at high temperatures, causing it to clog internal combustion engines and become partially oxidised into toxic acrolein (Mario et al., 2008). On the other hand oxygenated molecules such as methyl tertbutyl ether (MTBE, now banned in many US states) are valuable additives due to their antidetonant and octane-enhancing properties. In particular, glycerol tert-butyl ethers (GTBEs) are excellent additives and offer considerable potential for diesel and biodiesel reformulation (Liotta et al., 1994).

A mixture of 1,3-di-, 1,2-di- and 1,2,3-tri-tert-butyl glycerol, which is soluble in nonpolar fuels, can be incorporated into standard diesel fuel containing 30–40% aromatics. This provides significantly reduced emissions of particulate matter, hydrocarbons, carbon monoxide and unregulated aldehydes (Liotta et al., 1994). Oxygenated diesel fuels are of importance for both environmental compliance and efficiency of diesel engines. In general, the addition of these ethers has a positive effect on the quality of diesel fuel and assists in the reduction of fumes and particulates, oxides of carbon and carbonyl compounds in engine exhausts. Furthermore, in the case of biodiesel a limitation in its use is the cloud point, which is –16 °C for petroleum-based diesel but around 0 °C for biodiesel. The addition of ethers such as GBTEs decreases the cloud point of diesel fuels (Noureddini et al., 2001). Remarkably, glycerol ethers can also considerably reduce the NOx emissions generated from the burning of pulverized coal in heat-producing units (D. B. Appleby et al., 2007). As already mentioned, according to an EU directive 5.75%of the total amount of fuel consumed in the Union by 2010 will have to originate from renewable sources. In Germany alone this would be equivalent to 30 million ton of biodiesel, and hence 3 million tonnes of glycerol, or 10 million tonnes of GTBEs. If achieved, this could be easily absorbed by the market since large quantities of isobutylene are already available due to its use as a starting material for MTBE, which although banned in California, New York and 18 other US states is still allowed in the EU. Glycerol alkyl ethers are readily synthesized by etherification (O-alkylation) of alkenes, particularly isobutylene in the presence of an acid catalyst at temperatures from 50 to 150 °C and at molar ratios of glycerol: isobutylene of 1: 2 or above (Gupta et al., 1995 and Behr and Obendorf et al., 2002). The yield can be maximized by optimizing the reaction conditions, in particular the temperature, molar ratio, and type and amount of catalyst. Initially the reaction mixture consists of a two-phase system, one being a glycerol-rich polar phase (containing the acidic catalyst and mono-tert-butyl glycerol ether), and the other being an olefin-rich hydrocarbon phase, also containing glycerol diethers and triether.

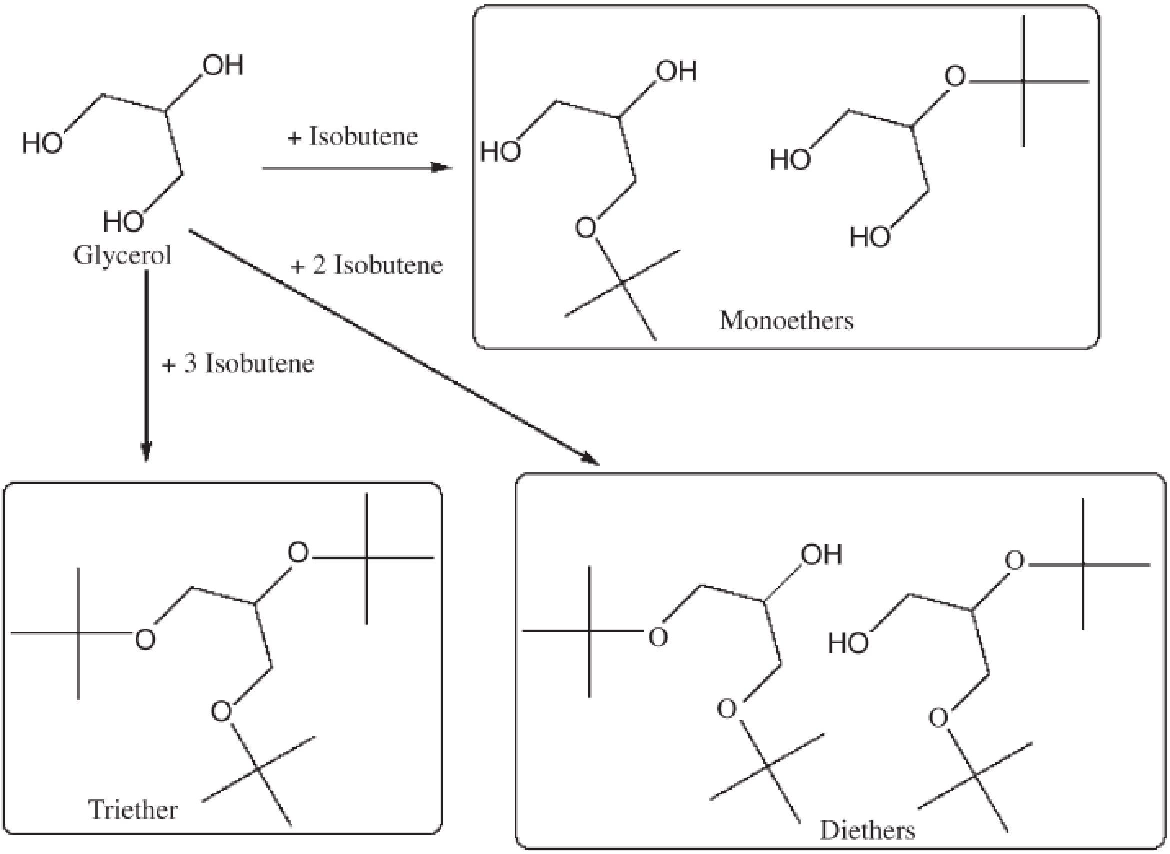


Figure 2.2 Reaction products from the tert-butylation of glycerol with isobutene. (K. Klepacova et al., 2005)

As the reaction proceeds the products accumulate in one or other of the phases according to their solubility. During the reaction the solubility changes as the concentration of reaction products increases. At a glycerol conversion of about 60–70% the two phases amalgamate to form a single phase. The etherification of glycerol with isobutylene in the liquid phase without solvent, catalyzed by strongly acidic resins such as Amberlyst or large-pore zeolites, affords complete conversion of glycerol (K. Klepacova et al., 2005). Macroreticular resins are highly active due to their large pore diameter, which remains constant due to the high level of crosslinking after swelling in the reaction medium. Complete conversion of glycerol, with selectivity to di- and triethers greater than 92%, is easily obtained over Amberlyst 35 at 60 °C. In general, five ethers are formed in the process and optimal selectivity toward ethers is achieved at 80°C with an isobutene: glycerol molar ratio around 3: 1 (Karinen et al., 2006). The mono, di-and tri-tert-butyl ether reaction products have been characterized using MS, NMR, IR and Raman molecular spectroscopy (M. E. Jamro´ z et al., 2007). A drawback to the use of Amberlyst ionexchange resins is that the methanol, salt and water present in crude glycerol originating from biodiesel production must be removed in order to avoid poisoning the catalyst (Noureddini et al., 1998).

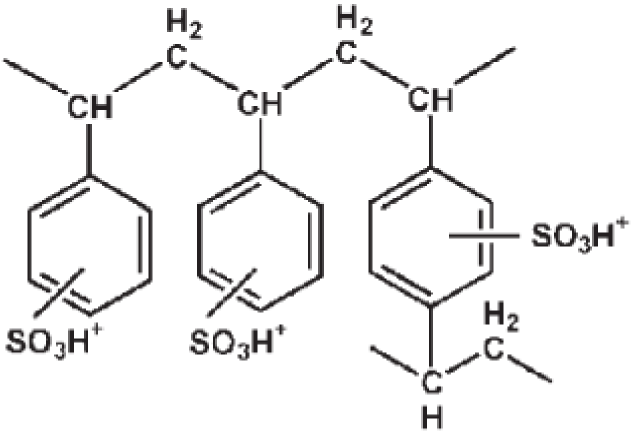


Figure 2.3 Amberlyst 35 is an excellent catalyst for glycerol alkylation with isobutene, but it requires the use of pure glycerol. (Noureddini et al.,1998).

2.5 Oxygenated Compound

Oxygenates are compounds containing oxygen in a chain of carbon and hydrocarbon atoms. Their structure provides a reasonable anti-knock value, thus they can be utilized to replace aromatics in gasoline. In addition, the advantage of using the oxygenate agents is to reduce smog-forming tendencies of the exhaust gases. Alcohols have been used in gasoline since the 1930s while MTBE was first used in commercial gasoline in Italy in 1973 and in the US by ARCO in 1979. In 1996, over 95% of gasoline used in California was blended with MTBE. Oxygenate can be derived from fossil fuels such as methanol (MeOH), methyl tertiary butyl ether (MTBE), tertiary amyl methyl ether (TAME), or from biomass such as ethanol (EtOH), ethyl tertiary butyl ether (ETBE) and tert amyl ethyl ether (TAEE). Oxygenates are beneficial to gasoline function in two ways. Firstly, they have higher blending octane number, so they can replace high octane aromatics in the fuel. These aromatics are responsible for disproportionate amounts of CO and HC exhaust emissions. This is called the “aromatic substitution effect”. Oxygenates can also be used in engines without sophisticated engine management systems to move to the lean side of stoichiometry, thus reducing emission of CO (2% oxygen can reduce CO by 16%) and HC (2% oxygen can reduce HC by 10%).

2.6 Catalysts

Ion exchange resin

An ion exchange resin is an insoluble polymeric matrix or support structure, usually supplied as white or yellowish bead (shown in Figure 1) and with electrically charged sites at which one ion may replace another in a process called ion exchanging.

Figure 2.4 Ion exchange resin beads (Thipsunet, 2006)

Physical structure of resin

Generally, ion exchange resin can be manufactured from a material which has basic requirements of ion exchange bead. It must be insoluble under normal operating condition, and must be uniform dimension form of sphere. The swelling and contraction of resin bead during exhaustion and regeneration must not cause the bead to burst. In addition, the active site must be permanently attached to the bead. Usually, there are two physical structures of resin; i.e. micro porous and macro porous resin.

Micro porous resin (also called gel resin) is generally a translucent and homogenous crosslink polymer. It does not have permanent pore structure. Therefore, it has no measurable porosity, generally considered to be quite small, usually less than 30 ^{o}A and referred as gellular pore or molecular pores. The pore structure is determined by the distance between the polymer chains and crosslinks which depends on the % crosslinkage of the polymer, the polarity of the solvent, and the operating condition. Normally, it has higher operating efficiencies and lower cost than macro porous resin.

Macro porous resin (also called macro reticular resin) is a large multichannel porous structure and it can be made of two continuous phases; a continuous pore phase and a continuous gel polymeric phase which is structurally composed of small spherical micro gel particles agglomerated together to form cluster, which are fastened together at the interfaces and form inter-connecting pore. It not only has high effective surface area to facilitate ion exchange process and to give access to the exchange site for large ion but also give better physical stability, primarily because of its sponge like structure which gives more stress relief, and better oxidation resistance. Unfortunately, the multi-channel porous structure like sponge allows the active portion of the bead to contain a high level of DVB crosslinking without affecting the exchange kinetics; it means that it has a lower capacity because the beads contain less exchange sites. The “pore” can take up to 10 to 30 % of the polymer which is the reason to reduce the ion exchange capacity proportionately.

Usually, synthetic ion exchange resins are cast as porous beads with considerable external and pore surface where ions can attach. Whenever there is a great surface area, adsorption plays a role. If a substance is adsorbed to an ion exchange resin, no ion is liberated. While there are numerous functional groups that have charge, only a few are commonly used for principle ion exchange resins. These are:

1. Strongly acidic; sulfonic acid groups $-SO_3H$ which is strongly ionized to $-SO_3$
2. Strongly basic; $-NR_3^+$ that has a strong, permanent charge. (R stands for some organic group)
3. Weakly acidic; carboxylic acid groups $-COOH$ which is weakly ionized to $-COO^-$
4. Early basic; $-NH_2$ that weakly attracts protons to form NH_3^+, -secondary and tertiary amines that also attract protons weakly

These groups are sufficient to allow selection of a resin with either weak or strong positive or negative charges.

Chemical structure of resin

Commonly, there are two basic types of chemical structures; styrene and acrylic matrix material while divinylbenzene (DVB) is still used as a crosslinker in these matrixes. The acrylic based material is straight chained hydrocarbons based on polyacrylate and polymethacrylate. The active exchange site of acrylic differing from the styrene is part of the physical structure. The acrylic based material is advantageous in application where organics are presented because it does not foul nearly as much as a styrene based material. However, when an acrylic resin chemically degrades, which is the weak link beyond the physical structure. Furthermore, when an acrylic resin oxidizes, it will swell and become mushy, therefore is usually limited to industrial application. Presently, most ion exchange resins are manufactured by using styrene as the matrix material.

Ion exchange resin based on the copolymerization of styrene and DVB the most commonly used in the world today has been developed since 1944 by an American scientist,
D' Alelio and is referred to as being gellular in structure. DVB is the cross linking agent, link together the back bone of styrene polymer contributed to three dimension of the network, fashion it insoluble and determines to what extent the resin is free to swell and shrink. The term "Cross linkage" in a styrene - DVB resin refers to the fraction of DVB. For example, 8 percent crosslinkage means that it contain 92 percent of styrene and 8 percent of DVB. Resins are available today with a DVB content of from 2 to 20% or higher. Higher DVB content gives the bead additional strength but the additional crosslinking can hinder kinetic by making the bead too resistant to the shrinking when in contact with non polar solvent and to swelling when charging from one ionic form to another form, during normal operating.

Physical and chemical properties of ion exchange resins

Since ion exchange resin is the copolymer of styrene and DVB, it has most of ideal network properties consisting of a structure resistant to breakage, mechanical wear, oxidation or reduction, uniform of shape in small spheres with good hydraulic properties and insoluble in solvents. The properties of resin depend on the crosslinkage of styrene and DVB and the particle size of resin. These factors are important parameters to describe several properties; that is, moisture content, capacity, equilibration rate, selectivity for various ions, porosity, and flow rate of solution and physical stability.

1. Crosslinkage

The amount of crosslinking depends on the proportions of different monomers used in the polymerization step. Practical ranges are 4 % to 16 %. Resins with very low crosslinking tend to be watery and change dimensions markedly depending on which ions are bound. Properties that are interrelated with crosslinking are:

- Moisture Content

A physical property of the ion exchange resins that varies with changes in crosslinkage is the moisture content of the resin. For example, sulfonic acid groups attract water, and this water is tenaciously held inside each resin particle. The quaternary ammonium groups of the anion resins behave in a similar manner.

- Capacity

The total capacity of an ion exchange resin is defined as the total number of chemical equivalents available for exchange per some unit weight or unit volume of resin. The capacity may be expressed in terms of mole-equivalents per unit mass of dry resin or in terms of mole-equivalents per unit volume of wet resin.

Generally, the resins have the higher crosslinked, the more difficult to introduce additional functional groups. Sulfonation is carried out after the crosslinking has been completed and the sulfonic acid groups are introduced inside the resin particle as well as over its surface. Likewise, the quaternary ammonium groups are introduced after the polymerization has been completed and they also are introduced both inside the particle as well as on its surface. Fewer functional groups can be introduced inside the particles when they are highly crosslinked and hence the total capacity on a dry basis drops slightly.

This situation is reversed when a wet volume basis is used to measure the capacity on a resin. Although fewer functional groups are introduced into a highly crosslinked resin, these groups are spaced closer together on a volume basis because the volume of water is reduced by the additional crosslinking. Thus the capacity on a wet volume basis increases as cross-linking increases.

- Equilibrium Rate

Ion exchange reactions are reversible reactions with equilibrium conditions being different for different ions. Crosslinkage has a definite influence on the time required for an ion to reach equilibrium. An ion exchange resin that is highly crosslinked is quite resistant to the diffusion of various ions through it and hence, the time required for reaching equilibrium is much longer. In general, the larger ion or molecule diffusing into an ion exchange particle, or the more highly crosslinked the polymer, the longer the time is required to reach equilibrium conditions.

Copolymers of styrene containing low amounts of divinylbenzene (1- 4%) are characterized as having high degree of permeability, large amount of moisture, and high rate to reach equilibrium, but poor physical stability, and selectivity. However, ability to accommodate larger ions is increased. Copolymers of styrene containing high amounts of divinylbenzene (12-16%) exhibit characteristics in the opposite direction.

2. Particle Size

The physical size of the resin particles is controlled during the polymerization step. Screens are used to sieve resins to get a fairly uniform range of sizes. Mesh sizes in Table 2.4 refer to U.S. standard screens. A higher mesh number means more and finer wires per unit area and thus a smaller opening.

Table2.3 Diameter of particles related to mesh range (Thipsunet, 2006)

Mesh Range	**Diameter of particles (Inches)**	**Diameter of particles (Micrometers)**
20 - 50	0.0331-0.0117	840-297
50 - 100	0.0117-0.0059	297-149
100 - 200	0.0059-0.0029	149-74
200 - 400	0.0029-0.0015	74-38
minus 400	< 0.0015	< 38

For the equilibration rate, the particle size of an ion exchange resin influences the time required to establish equilibrium conditions. There are two types of diffusion that must be considered in anion exchange equilibrium. The first is called film diffusion or the movement of ions from a surrounding solution to the surface of an ion exchange particle. The second is called internal diffusion which is the movement of ions from the surface to the interior of an ion exchange particle. Film diffusion is usually the controlling reaction in dilute solutions whereas internal diffusion is controlling in more concentrated solutions. The particle size of an ion exchange resin affects both film diffusion and internal diffusion. A fine mesh particle presents more surface area for film diffusion and also contains less internal volume through which an ion must diffuse. A decrease in particle size thus shortens the time required for equilibrium condition.

Amberlyst 16 wet

Amberlyst 16 wet is a bead form, macroreticular, sulfonic acid, ion exchange resin, developed particularly for heterogeneous catalysis. The macroreticular structure and large pore diameter of Amberlyst 16 wet ensures that it has excellent activity in polar organic systems. The sulfonic acid groups of Amberlyst 16 are more resistant to thermal degradation than other ion exchange catalysts, allowing it to be used economically at higher temperature. Amberlyst 16 is mainly used in the esterification and phenol alkylation processes.

Table 2.4 Typical Properties of Amberlyst 15 and Amberlyst 16 (ROHM and HAAS)

Physical form	Opaque beads
Ionic form as shipped	Hydrogen
Concentration of active sites	≥ 1.7 eq/L
	≤ 4.8 eq/kg
Moisture holding capacity	52 to 58 % (H^+ form)
Shipping weight	780 g/L (48.7 lbs/ft^3)
Particle size	
Harmonic mean size	0.600 to 0.800 mm
Uniformity coefficient	≤ 1.6
Fines content	⟨ 0.300 mm : 1.0 % max
Coarse beads	⟩ 1.180 mm : 10.0 % max

Amberlyst 15

Amberlyst 15 is astrongly acidic, sulfonic acid, macroreticular polymeric resin based on crosslinked styrene divinylbenzene copolymers. Its continuous open pore structure and excellent physical, thermal and chemical stability makes it the resin of choice in many applications. It also possesses a greater resistance to oxidants with such as chlorine, oxygen and chromates than most other polymeric resins. Amberlyst 15 can be used directly in aqueous systems or in organic media after conditioning with a water miscible solvent.

Zeolites

Zeolites are crystalline aluminosilicates with fully cross-linked open framework structures made up of corner-sharing SiO_4 and AlO_4 tetrahedral. The first zeolite, stibnite, was discovered by Cronstedt in 1756, who found that the mineral loses water rapidly on heating and thus seems to boil. The name “Zeolite” comes from the Greek words zeo (to boil) and lithos (stone). A representative empirical formula of zeolite is $M_{2/n}.Al_2O_3.xSiO_2.yH_2O$, where M represents the exchangeable cation of valence n. M is generally a group I or II ion, although other metal, non-metal and organic cations may also balance the negative charge created by the presence of Al in the structure. The framework may contain cages and channels of discrete size, which are normally occupied by water. In addition to Si^{4+} and Al^{3+}, other elements can also be present in the zeolitic framework. They do not need to be isoelectronic with Si^{4+} and Al^{3+}, but must be able to occupy framework sites. Aluminosilicate zeolites display a net negative framework charge.

Structure of zeolite

The framework of a zeolite is based on an extensive three-dimensional network in which the polyhedral sites, usually tetrahedral, are linked by oxygen atoms. The crystalline framework contains cages and channels of discrete size and 3-30 $\overset{o}{A}$ in diameter. The primary building unit of a zeolite is the individual tetrahedral unit. The T atom (T = Si or Al) belonging to a TO_4 tetrahedron is located at each corner, but the oxygen is located near the mid-points of the lines joining each pair of T atoms. The topology of all known zeolite framework types can be described in terms of a finite number of specific combinations of tetrahedral called “secondary building units”(SBU’s). A zeolite framework is made up of one type of SBU only.

Description of the framework topology of a zeolite involves “tertiary” building units corresponding to different arrangements of the SBU’s in space. Various alternative ways have been proposed. The framework may be considered in terms of large polyhedral building blocks forming characteristic cages. For example, sodalite, zeolite A and zeolite Y can all be generated by the truncated octahedron known as the beta-cage.

An alternative method of describing extended structures uses two-dimensional sheet building units. Sometimes various kinds of chains can be used as the basis for constructing a zeolite framework.

Properties of zeolite

The most important application of zeolite is used a catalyst. Zeolites combine high acidity with shape selectivity, high surface area, and high thermal stability and have been used to catalyze a variety of hydrocarbon reactions, such as cracking, hydrocracking, alkylation and isomerisation. The reactivity and selectivity of zeolites as catalysts are determined by the active sites brought about by a charge imbalance between the silicon and aluminium atoms in the framework. Each framework aluminium atom induces a potential active acid site. In addition, purely siliceous and $AlPO_4$ molecular sieves have Brønsted acid sites whose weak acidity seems to be caused by the presence of terminal OH bonds on the external surface of crystal. Shape selectivity, including reactant shape selectivity, product shape selectivity or intermedia shape selectivity plays a very important role in zeolite catalysis. The channels and cages in a zeolite are similar in size to medium-sized molecules. Different sizes of channels and cages may therefore promote the diffusion of different reactants, products or intermedia species. High crystallinity and the regular channel structure are the principal features of zeolite catalysts. Reactant shape selectivity results from the limited diffusivity of some of the reactants, which cannot effectively enter and diffuse inside the crystal. Product shape selectivity occurs when slowly diffusing product molecules cannot rapidly escape from the crystal, and undergo secondary reactions. Restricted intermedia shape selectivity is a kinetic effect arising from the local environment around the active site: the rate constant for a certain reaction mechanism is reduced if the necessary intermedia are too bulky to form readily.

Zeolites are selective, high-capacity adsorbents because of their high intracrystalline surface area and strong interactions with adsorbates. Molecules of different size generally have different diffusion properties in the same molecular sieve. Molecules are separated on the basis of size and structure relative to the size and geometry of the apertures of zeolite. Zeolites adsorb molecules, in particular those with a permanent dipole moments, and exhibit other interactions not found in other adsorbents. Different polar molecules have a different interaction with the zeolite framework, and may thus be separated by a particular zeolite. This is one of the major uses of zeolites. An example is the separation of N_2 and O_2 in the air on zeolite A, by exploiting different polarities of the two molecules.

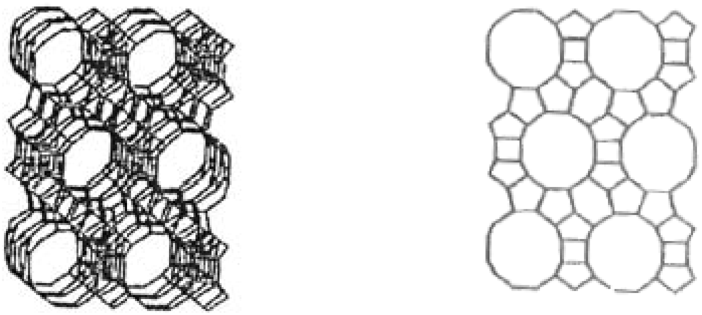
Zeolites with low Si/Al ratios have strongly polar anionic frameworks. The exchangeable cation creates strong local electrostatic fields and interacts with highly polar molecules such as water. The cation-exchange behaviour of zeolites depends on (1) the nature of the cation species - the cation size (both anhydrous and hydrated) and cation charge, (2) the temperature, (3) the concentration of the cationic species in the solution, (4) the anion associated with the cation in solution, (5) the solvent (most exchange has been carried out in aqueous solutions, although some works have been done in organics) and (6) the structural characteristics of the particular zeolite.

Solid heterogeneous catalyst: Beta zeolite

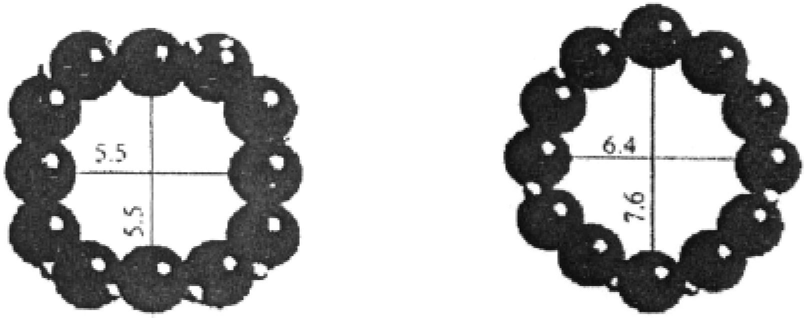
Beta zeolite was initially synthesized by Wadlinger *et al*. (1995) using tetraethylammonium hydroxide as an organic template. The chemical composition of beta zeolite is $(TAE,Na)_2O.Al_2O_3.5\text{-}100SiO_2.4H_2O$

Beta zeolite is a large pore, high silica and crystalline aluminosilicate.

The framework and the pore structure of the zeolite have several unique features. It is the only large pore zeolite to have chiral pore interactios. The high silica zeolites are attractive catalytic materials because of their thermal and hydrothermal stabilities, acid strength, and good resistance for deactivation and hydrophobicity. The pore structure of beta zeolite consists of 12 membered rings interconnected by cages formed by the interaction of channels. The dimension of pore opening in the linear channel is 5.7 ^{o}A x 7.5 ^{o}A. The tortuous channel system consists of the interactions of two linear channels of approximate dimensions of 5.6 ^{o}A x 6.5 ^{o}A. Beta zeolite has a total pore volume around 0.2 ml/g. The above characteristics make beta zeolite a potential candidate for a variety of hydrocarbon conversion reactions. The framework structures of beta zeolite are shown in Figure 2.5.



(a) framework structure (b) framework projection



(c) tortuous channel (d) straight channel

Figure 2.5 structure of beta zeolite (Thipsunet, 2006)

2.7 Group contribution method

Physical and thermodynamic properties of gases and liquids are of vital concern to the chemical engineer, who is involved in research, in development, in plant design, or in production. But for many compounds of interest to the chemical engineer, the only data available such as the molecular weight and the boiling point and for some of newer, more exotic compounds, even the boiling point may not have been reported. Even for well-known compounds, the data available will often not cover the region of interest to the chemical engineer. It is thus not surprising that in recent years literally thousands of investigated which present methods of estimating a variety of properties. Many of the method are base on theoretical considerations and allow the user to calculate one set of properties from another set already known. Others require only acknowledge of the structure of the compound under consideration and use empirically derived contributions for various atomic or function subgroups within the molecule. Such contributions are then manipulated algebraically to estimate the required output properties. “Structural increment” method are extremely useful if no other property data exist for the compound, since calculated output properties can then be in other methods to estimate a variety of other properties.

2.7.1 Joback’s method

Joback’s (1984) reevaluated Lydersen’s group contribution method scheme, added several new functional groups, and determined new contribution values. The relations for calculations properties are:

$$T_c(K) = T_b[0.584 + 0.965\{\sum_k N_k(tck)\} - \{\sum_k N_k(tck)\}^2]^{-1} \tag{2.1}$$

$$P_c(bar) = [0.113 + 0.0032N_{atoms} - \sum_k N_k(pck)]^{-2} \tag{2.2}$$

$$T_b = 198 + \sum_k N_k(tbk) \tag{2.3}$$

$$\Delta G_f^0 = 53.88 + \sum_k N_k(gfk) \tag{2.4}$$

Those the contributions are indicated as tck, pck and vck. The group identities and Joback’s value for contributions to the critical are listed in Appendix A. For calculation of Tc, the value of the normal boiling point, Tb, is needed.

2.7.2 Gani’s method

Constantinou and Gani (1994) developed an advance group contribution method on the UNIFAC group but they allow for more sophisticated of the desired properties and also for contributions at a “second order” level. The functions give more flexibility to the correlation while the second order partially overcomes the limitation of UNIFAC which cannot distinguish special configurations such as isomers, multiple groups located close together, resonance structures, etc., at the "first order". The general CG formulation of a function f [F] of a property F is

$$F = f[\sum_k N_k (F_{1i}) + W \sum_j M_j (F_{2j})] \tag{2.5}$$

Where f can be a linear or nonlinear function, Nk is the number of First-order groups of type k in the molecule; F_{1k} is the contribution for the First-Order group labeled 1k to the specified properties, F; M_j is the number of second-order group of type j in the molecular; and F_{2j} is the contribution for the second-order group labeled 2j to the specified property, F. The value of W is set to zero for first-order calculations and set to unity for second-order calculations. For the properties, the CG formulations are;

$$Tc(K) = 181.128 \ln[\sum_k N_k (tc1k) + W \sum_j M_j (tc2j)] \tag{2.6}$$

$$Pc(bar) = [\sum_k N_k (pc1k) + W \sum_j M_j (pc2j) + 0.10022]^{-2} + 1.3705 \tag{2.7}$$

$$Tb(K) = 204.359 \ln[\sum_k N_k (tb1k) + W \sum_j M_j (tb2j)] \tag{2.18}$$

$$\Delta G_f^o (kJmol^{-1}) = -14.83 + [\sum_k N_k (gf1k) + W \sum_j M_j (gf2j)] \tag{2.9}$$

The error of this method is large when it is applied with calculations of low carbon atom and second-order is applied. But the CG method can be quite reliable for the formation properties, especially for species with three or more carbon atoms. The functional groups from Gani's group contribution are listed in Appendix B.

2.7.4 Benson's method

Benson and coworkers have developed the technique for estimation for thermodynamic properties. There are several references to Benson's work such as CHETAH program. Benson's method is detailed of the contribution of bonding arrangements that chosen groups can have with every other type of group or atom except hydrogen. Thus the method involves next-nearest neighbor interactions.

The values from the Benson group can be assumed directly to obtain standard enthalpy of formation ($\Delta H_f^o(298.15K)$), and heat capacity ($C_p^o(T)$) values. However, obtaining $S_f^o(298.15)$ also requires taking molecular symmetry in to account. Finally, obtaining $\Delta G_f^o(298.15)$ requires subtracting the entropy of the elements. The relations are;

$$\Delta H_f^o(298.15K) = \sum_k N_k(\Delta H_{fk}^o) \tag{2.10}$$

$$S^o(298.15K) = \sum_k N_k(S_k^o + S_s^o) + S_s^o \tag{2.11}$$

$$S_{el}^o(298.15K) = \sum_e v_e(S_e^o) \tag{2.12}$$

$$\Delta G_f^o(298.15K) = \Delta H_f^o(298.15K) - 298.15[S^o(298.15K) - S_{el}^o(298.15K)] \tag{2.13}$$

The Benson's group contribution values are listed in appendix C. The sample entropy, S_s^s is independent of T and given by

$$S_s^o = R\ln(N_{oi}) - R\ln(N_{ts}) \tag{2.14}$$

Where N_{oi} is the number of structural isomers of the molecule and N_{ts} is the total symmetry number. Normally, N_{oi} =1 so it makes no value in equation (2.14). The two cases can be non unit values. The first is when there is a plane of symmetry where the atoms can form mirror image arrangements (optical isomers) so that the atom in the plane has asymmetric substitutions. For example, the four atoms (H, F, Cl, I) bonded to the carbon in CHFClI can be arranged in two distinct ways, so its N_{oi} =2. The second way for N_{oi} to be different from unity is if an otherwise symmetrical molecule is frozen by steric effect onto an asymmetrical conformation. For example, 2, 2', 6, 6'-tetramethylbiphenyl cannot rotate about the bond between the two benzene rings due to its 2, 2' steric effects. Therefore, the plane of the ring can have two distinct arrangements (N_{oi} =2) which must be included in the entropy calculation. If the desired species is the racemic mixture (equal amounts of the isomers), each asymmetric center contributes two to N_{oi}, but if the species is a pure isomer, N_{oi} =1.

To obtain N_{ts}, one multiplies the two distinct types of indistinguish ability that can occur: "internal" designated N_{is}, and "external" designated N_{es}. The value of N_{is} can be found by rotating terminal groups about their bonds to interior groups. An example is methyl (-CH_3) which has three indistinguishable conformations (N_{ts}= 3) and phenyl which has N_{ts}=2. The value of N_{es} comes from diatomic have N_{es} = 2 rotation from about their bond axis, benzene has N_{es} = 6 from rotation about its ring center, etc. Finally N_{ts} is found form;

$$N_{ts} = N_{es} \bullet \prod_{k=term} (N_{is})_k \tag{2.15}$$

The UNIFAC method for estimation of activity coefficient depends on the concept that a liquid mixture may be considered as a solution of the structural units from which the molecules are formed rather than a solution of the molecules themselves. These structural units are called subgroups. A number, designated k, identifies each subgroup. The relative volume R_k and relative surface area Q_k are properties of the subgroups. When it is possible to construct a molecule from more than one set of subgroups, the set containing the least member of different subgroups is the correct set. The great advantage of the UNIFAC method is that a relatively small number of subgroups combine to form a very large number of molecules.

Activity coefficients depend not only on the subgroup properties R_k and Q_k, but also on interactions between subgroups. Here, similar subgroups are assigned to a main group. The designations of main groups, such as "CH_2", "ACH", etc., are descriptive only. All subgroups belonging to the same main group are considered identical with respect to group interactions. Therefore parameters characterizing group interactions are identified with pairs of main groups.

The UNIFAC method is based on the UNIQUAC equation which treats $g \equiv G^E / RT$ as comprised of two additive parts, a combinatorial term g^C to account for molecular size and shape differences, and a residual term g^R to account for molecular interactions:

$$g = g^C + g^R \quad * \tag{2.16}$$

***** equation reference (Bruce E. Poling, John M.Prausnitz, John P. O'Connell, The properties of gases and liquids, Mcgraw-Hill, Fourth edition)

Function g^C contains pure-species parameters only, whereas function g^R incorporates two binary parameters for each pair of molecules. For a multi-component system,

$$g^C = \sum x_i \ln \frac{\phi_i}{x_i} + 5 \sum q_i x_i \ln \frac{\theta_i}{\phi_i} \tag{2.17}$$

And

$$g^R = - \sum q_i x_i \ln(\sum \theta_j \tau_{ji}) \tag{2.18}$$

Where

$$\phi_i = \frac{x_i r_i}{x_j r_{j\ i}} \tag{2.19}$$

And

$$\theta_i = \frac{x_i q_i}{x_j q_{j\ i}} \tag{2.20}$$

Subscript i identifies species, and j is a dummy index; all summations are over all species. Note that $\tau_{ji} \neq \tau_{ii}$; however, when $i = j$, then $\tau_{jj} = \tau_{ii} = 1$. In these equations r_i (a relative molecular volume) and q_i (a relative molecular surface area) are pure-species parameters. The influence of temperature on g enters through the interaction parameters τ_{ji} of Eq. (2.19), which are temperature dependent:

$$\tau_{ji} = \exp\frac{-(u_{ji} - u_{ii})}{RT} \qquad (2.21)$$

Parameters for the UNIQUAC equation are therefore values of $(u_{ji} - u_{ii})$.

An expression for $\ln\gamma_i$ is applied to the UNIQUAC equation for g [Eqs. (2.17) to (2.19)]. The result is given by the following equations:

$$\ln\gamma_i = \ln\gamma_i^C + \ln\gamma_i^R \qquad (2.21)$$

$$\ln\gamma_i^C = 1 - J_i + \ln J_i - 5q_i(1 - \frac{J_i}{L_i} + \ln\frac{J_i}{L_i}) \qquad (2.22)$$

And

$$\ln\gamma_i^R = q_i(1 - \ln s_i - \sum\theta_j\frac{\tau_{ij}}{s_j}) \qquad (2.23)$$

Where in addition to Eqs (2.20) and (2.21)

$$J_i = \frac{r_i}{\sum x_j r_j}S \qquad (2.24)$$

$$L_i = \frac{q_i}{\sum x_j q_j}S \qquad (2.25)$$

$$s_i = \sum\theta_l\tau_{li} \qquad (2.26)$$

Again subscript i identifies species, and j and l are dummy indices. All summations are over all species, and $\tau_{ij} = 1$ for i=j. Values for the parameters $(u_{ij} - u_{jj})$ are found by regression of binary VLE data.

When applied to a solution of groups, the activity coefficients are calculated by:

$$\ln\gamma_i = \ln\gamma_i^C + \ln\gamma_i^R \qquad (2.27)$$

When

$$\ln\gamma_i^C = 1 - J_i + \ln J_i - 5q_i(1 - \frac{J_i}{L_i} + \ln\frac{J_i}{L_i}) \qquad (2.28)$$

And

$$\ln \gamma_i^R = q_i[1-(\theta_k \frac{\beta_{ik}}{s_k} - e_{ki} \ln \frac{\beta_{ik}}{s_k})] \tag{2.29}$$

The quantities J_i and L_i are given by:

$$J_i = \frac{r_i}{x_j r_j} \tag{2.30}$$

$$L_i = \frac{q_i}{x_j q_j} \tag{2.31}$$

In addition, the following definition of parameters in Eqs. 2.28 and 2.29 apply:

$$r_i = v_k^{(i)} R_k \tag{2.32}$$

$$q_i = v_k^{(i)} Q_k \tag{2.33}$$

$$e_{ki} = \frac{v_k^{(i)} Q_k}{q_i} \tag{2.34}$$

$$\beta_{ik} = e_{mi} \tau_{mk} \tag{2.35}$$

$$\theta_{ik} = \frac{x_i q_i e_{ki}}{x_j q_j} \tag{2.36}$$

$$s_k = \theta_m \tau_{mk} \tag{2.37}$$

$$\tau_{mk} = \exp(\frac{-a_{mk}}{T}) \tag{2.38}$$

Subscript i identified species, and j is a dummy index running over all species. Subscript k identifies subgroups, and m is a dummy index running over all subgroups. The quantity $v_k^{(i)}$ is the number of subgroups of type k in a molecule of species i. Values of the subgroup parameters R_k and Q_k and of the group interaction parameters, a_{mk} come from tabulation in the literature.

2.8 Aspen Plus

Aspen Plus is one of the components in the Aspen Engineering Suite. It is an integrated set of products designed specifically to promote best engineering practices and to optimize and automate the entire innovation and engineering workflow process throughout the plant and across the enterprise. It automatically integrates process models with engineering knowledge databases, investment analyses, production optimization and numerous other business processes. Aspen Plus contains data, properties, unit operation models, built-in defaults, reports and other features. Its capabilities develop for specific industrial applications, such as petroleum simulation.

Aspen Plus is easy to use, powerful, flexible, process engineering tool for the design, steady-state simulation and optimization of process plants. Process simulation with Aspen Plus can predict the behavior of a process using basic engineering relationships such as mass and energy balances, phase and chemical equilibrium, and reaction kinetic. Given reliable thermodynamic data, realistic operating conditions and the rigorous Aspen Plus equipment models, actual plant behavior can be simulated. Aspen Plus can help to design better plants and to increase profitability in existing plants.

Features of Aspen Plus

1. Utilize the latest software and engineering technology to maximize engineering productivity through its Microsoft Windows graphical interface and its interactive client-server simulation architecture.
2. Contain the engineering power needed to accurately model the wide scope of real-world applications, ranging from petroleum refining to non-ideal chemical systems containing electrolytes and solids.
3. Support scalable workflow based upon complexity of the model, from a simple, single user, process unit flow sheet to a large, multi-engineer developed, multi-engineer maintained, plant-wide flow sheet.
4. Contain multiple solution techniques, including sequential modular, equation-oriented or a mixture of both, and allow as quick as possible solution times regardless of the application.

Benefits of Aspen Plus

1. Proven track record of providing substantial economic benefits throughout the manufacturing life cycle of a process, from R&D through engineering and into production.

2. Allow users to leverage and combine the power of sequential modular and Equation-oriented techniques in a single product, potentially reducing computational times by an order of magnitude while at the same the increasing the functionality and suability of the process model.

3. Complete effectively in an exacting environment to remain competitive in process currently industries it is necessary to do more, often with smaller staffs and more complex process.

CHAPTER III

LITERATURE REVIEWS

This chapter contains the research reviews of etherification of glycerol and etherification of reactive olefins with alcohol in both experiment and simulation. The reaction that possible to be occurred is etherification.

3.1 Gasoline octane improvement and etherification

The isomerization reaction one of this major process for octane improvement. The octane rating of straight run gasoline n-paraffins eas increased by isomerized to branched isoparaffins. The isomerized is major process for octane improvement. This must be specified process with high yields and high selectivity to high octane isomeric forms. Miller et al. (2001) had been reported the condition for isomerization can be occurred temperate range of 50 – 450 ^{o} C, but it favored of 100 ^{o} C. Later, they had been studied the isomerization of normal C4 and C5 olefins to convert larger atomic of reactive olefins. The conversion are greater than 50 wt% when use the catalyst such porous matrix material. Hardin et al. (1991) reported the process for convert linear C5 olefins to correspond of the same carbon using hydrogen with catalyst material. This process showed that the conversion of olefins level at least 50 wt% at temperature 150 to 600 ^{o}C.

Cruze et al. (2006) had studied the selectivity, conversion, yield, and kinetics of the liquid-phase dimerisation of 2-methyl-1-butene and 2-methyl-2- butene mixture catalysed by the acid resin Amberlyst 35 in a batch-stirred tank reactor in the temperature range 333–373 K in the presence of 10% mol alcohol content (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, t-butanol, and 1-pentanol). Dimers formation was favoured by increasing temperature and molecular weight of the alcohol, except for methanol. Secondary alcohols showed dimers formation more than primary alcohols did, and for t-butanol, neither ether nor dimers formation was detected. The obtained isomeric mixture of diisoamylenes consisted mainly of 3,4,4,5-tetramethyl-2-hexene, 2,3,4,4-tetramethyl-1-hexene, and 3,4,5,5-tetramethyl-2-hexene. LHHW- and ER-type kinetic models were derived for the dimerisation reaction, and their parameters were estimated by fitting experimental data. The best kinetic model was that in which three active sites took part in the rate-limiting step of dimerisation, with apparent activation energy for the dimerisation reaction in the range of 34–53 kJ / mol.

Bricout et al. (1998) had reported the nickel catalyzed isomerization of olefins in a two-phase system is reported. Provided that the water-soluble ligand is properly tailored and that the Brönsted acid is suitably selected, the catalytic system appears relatively stable and high catalytic activity can be reached. Fan et al. (2004) had developed catalyst excellent olefin control for FCC gasoline without loss in octane number. The use of different catalysts supported on composite carriers. The content in triple-zeolite carriers was found to be an important factor affecting the acid properties, pore structure, and hence hydroisomerization and aromatization activities of the catalysts.The highest activity could be achieved with the ratio of Hb to HMOR of 2.5. The increase of HZSM-5 content was confirmed to degrade the overall performance of catalysts. Compared to the binary-zeolite, the triple-zeolite supported catalysts offered much higher activity and selectivity to arene, which played an important role in preserving gasoline octane number.

Conventionally, etherification is known as the reaction between iso-olefins and alcohol. Ethanol contain oxygen in there molecules therefore addition of oxygenated ether into gasoline can improve combustion none completely.

Paivi et al. (2003) had been studied effect of feed MeOH/2M1B molar ratio on the initial isomerization and etherification rates of 2-methyl-1-butene (2M1B) in a batch reactor. The initial reaction rates for etherification and isomerization increased when the MeOH/2M1B molar ratio decreased. Several kinetic formulations were tested to explain this new data and the data obtained in earlier studies. According to the statistics, a kinetic model based on three active sites gave the best fit, but it was discussed that the basic Langmuir-Hinshelwood mechanism might be more adequate. Linnekoski et al. (1997) reported etherification reaction of isoamylenes (2-methyl-1-butene, 2M1B, and 2-methyl-2-butene, 2M2B) with methanol, ethanol, and n-propanol was studied using a commercial ion-exchange resin as a catalyst. Initial reaction rates showed the different alcohols (methanol, ethanol, and 1-propanol) affected the isomerization rate but not the etherification rate. It was also found that the reaction rates have a constant value at stoichiometric or higher ETOH/2M1B mole ratios. A new model was developed to explain the obtained results. It was found that, the adsorption of ethanol and olefins is not competitive. Alcohol adsorbs first, and then olefins adsorb to the same site. A new kinetic model was developed according to this mechanism. This model describes the experimental results better at low alcohol contents. Apparent activation energies were obtained, and they were comparable to the earlier obtained values. Vora et al. (1997) reported the combination of an etherification process and a process for the isomerization of linear alkenes to isoalkenes uses an adsorptive separation zone for olefin and paraffin separation upstream of the MTBE unit to reduce olefin losses associated with the rejection of butanes. Production of butene-1 stream having a purity of at least 99 wt % at the second fraction.

Rihko et al. (1994) reported for the reactivity of isoamylene (IA) with EtOH for etherification. There are two isomers of IA i.e. 2-methyl 1-butene (2M1B) and 2-methyl 2-butene (2M2B). It was found that 2M1B was more reactive than 2M2B which is good agreement with other researches (Randriamahefa et al., 1988 and Safronov et al., 1989). Oktar et al. (1999) studied the etherification of isoamylene with ethanol catalyzed by Amberlyst 15 in a temperature range of 333-360 K. They reported the apparent reaction order of etherification reactions of C_5 reactive olefins and its activation energy in the presence of excess alcohol. It is also shown that the diffusion resistances may play an important role on the observed rates. Then a number of works have been performed to determine the reaction equilibrium constant and rate expression of the TAEE synthesis from IA and ethanol (Oktar et al., 1999) .

Zhang et al. (1995) had studied the kinetics of isomerization and etherification of C_6 olefins with ethanol catalyzed by Amberlyst 15 to produce 3-methyl-3-ethoxy-pentane (THEE). The kinetic rate expressions are based on the Langmuir-Hinshelwood-Hougen-Watson (LHHW) formalism involving a dual-site surface etherification reaction and a single-site surface isomerization reaction. The results showed the rate-limiting steps are single site of surface isomerization. Adsorption experiments also confirmed the negligibility of the adsorption terms of olefins and ether, but it was found that the neglect of the vacant sites is erroneous. The equilibrium conversion of THEE production was lower than that of MTBE, ETBE, and TAEE production because the presence of the isomerization among olefins isomer. The calculated standard Gibbs free energy of formation at 298.15K is -116.5 kJ/ mol.

Kitchaiya et al. (1996) studied etherification of isobutene (IB) and methanol catalyzed by acidic zeolite catalysts i.e., H-Beta zeolite and H-ZSM-5. MTBE yields of 85-90% can be reached with zeolite H-Beta as well as Amberlyst 15 with in 12 h. Zeolite H-Beta exhibited a higher activity than Amberlyst 15 at temperature range of 313-373 K, however, the acid resin is slightly more selective than the H-Beta zeolites.

Linnekoski et al. (1998) investigated simultaneous etherification and hydration reaction of IA. They also focused on water adsorption effect for TAEE formation by using an azeotropic mixture of ethanol and water as reagent using the L-H model as a kinetic model. It was observed that water is the essential inhibitor of TAEE formation. A slight amount of water can largely retard the IA conversion.

3.2 Glycerol utilization and etherification of glycerol

Pachauri et al. (2006) studied utilization of crude glycerol from biodiesel production. Glycerol is a by-product from biodiesel industry. As the biodiesel production is increasing exponentially, the crude glycerol generated from the transesterification of vegetables oils has also been generated in a large quantity. Despite of the wide applications of pure glycerol in food, pharmaceutical, cosmetics, and many other industries, it is too costly to refine the crude glycerol to a high purity, especially for medium and small biodiesel producers. Many research projects and studies have been conducted and innovative utilizations of the crude glycerol are under investigations. It will be beneficial to the research community as well as biodiesel industry in understanding the progress of glycerol for value-added applications and for reference in manipulating their own integrated plans for sustainable and profitable biodiesel production. This report summarizes the currently available studied such as 1,3-propanediol, 1,2 propanediol and polyglycerol esters production.

Clacens et al. (2001) studied selective etherification of glycerol. The catalyst synthesis is the impregnation of mesoporous solids with different basic elements type in order to make them active, selective and stable catalysts for the target reaction. The impregnation method gives important activity for the catalytic, which must be correlated to important active species incorporation. The highest selectivity of (di-+tri-) glycerol was obtained over macroporous catalyst prepared by caesium impregnation.

Barrault et al. (2004) studied in the selective etherification of glycerol to di- and triglycerol. This were consisted in the synthesis and the modification, by different techniques, of caesium containing mesoporous solids of the MCM-41 in order to make them active, selective and stable for the target reaction. That result shown the impregnation method gives the highest activity and relating to the selectivity of the modified mesoporous catalysts, the best values to (di- + tri-) glycerol (>90%) are obtained over solids prepared by the impregnating or the grafting methods. The cesium-impregnated catalysts can be reused without loss of selectivity.

Products from etherification of glycerol are glycerol alkyl ethers. Some studies are used isobutylene or other olefins as reactants with difference quality of product also. Most of glycerol alkyl ethers are mono-, di- and tri-ethers but only di- and tri-ethers are desired product for diesel fuel.

Noureddini et al. (1998) studied the etherification of glycerol with isobutylene. Etherification of glycerol with isobutylene can be effectively accomplished using Amberlyst-15 as catalyst under a variety of reaction conditions. The optimum conditions were determined to be at 80 ºC, catalyst loading > 5 wt%, 1-2 h of reaction time, and isobutylene to glycerol molar ratio of 3:1. Blends of mono-, di-, and tri-tertiary butyl ethers of glycerol are the products and dimers of isobutylene are the by-products. Lower temperatures (80 °C) under these conditions resulted in a higher concentration of di- and tri-ethers and lower by-product concentrations. No catalyst deactivation was observed at least for reaction times up to 30 h. The ethers of glycerol can be effectively added to methyl esters, providing a 5 °C reduction in cloud point and an 8% reduction in viscosity.

When glycerol is etherified with isobutene or tert-butyl alcohol, some or all of the hydroxyl groups in the glycerol molecule react. Thus, depending on the extent of etherification, up to five ether isomers may be formed. (as show in Figure 3.1): two monosubstituted monoethers (3-tert-butoxy-1,2-propanediol (3.1a) and 2-tert-butoxy-1,3-propanediol (3.1b)), two disubstituted diethers (1,3-di-tert-butoxy-2-propanol (3.1c) and

2,3-di-tert-butoxy-1-propanol (3.1d)) and one trisubstituted triether (1,2,3-tri-tert-butoxy propane(3.1e)).

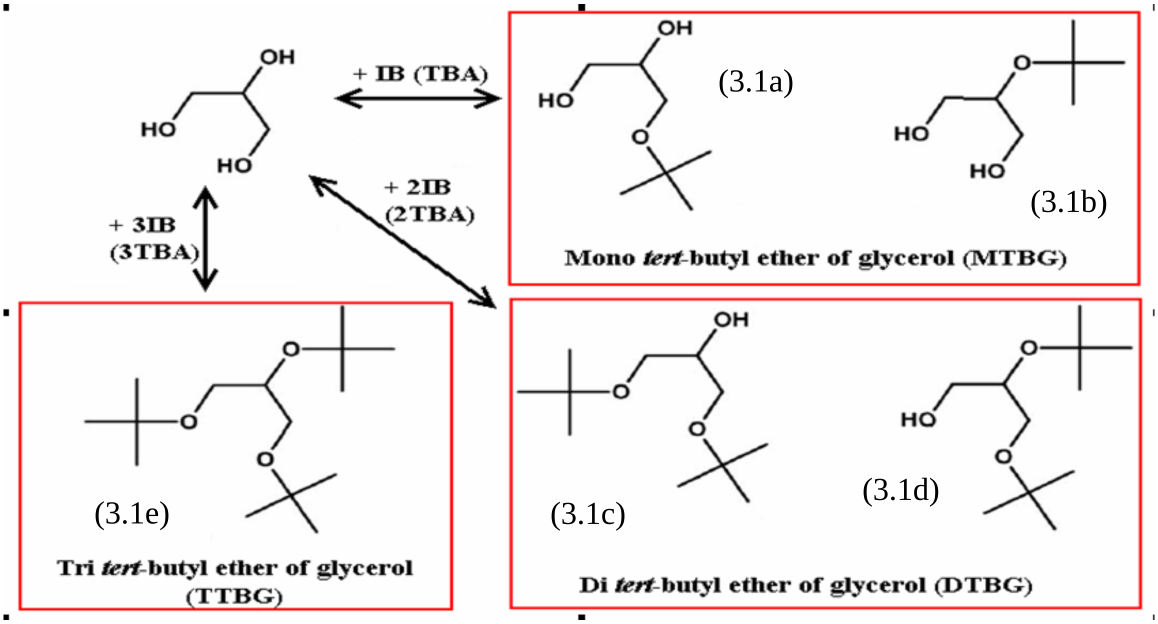


Figure3.1 Reaction scheme for the etherification of glycerol with isobutene. (Karinen *et al*. (2006))

Tert-Butyl ethers of glycerol with high content of di-ethers and especially tri-ethers are known as potential oxygenates to diesel fuels (diesel, biodiesel and their mixtures). These oxygenate ethers can reduce the emissions and mainly particulate matters. Karinen et al. (2006), etherified glycerol with isobutene in liquid phase with acidic ion exchange resin catalyst. Five product ethers and, as a side reaction, isobutene reacted to C_8–C_{16} hydrocarbons was obtained. The effect of the reaction conditions on the system was studied and conditions for optimal selectivity toward ethers were discovered near with isobutene/glycerol molar ratio of 3:1 at 80 °C. The reaction mixture separates into two liquid phases because glycerol and isobutene are insoluble in each other. Because of the separation, no samples were taken during the experiment, since it could not be guaranteed that the sample would well represent the reaction mixture and its phases. After the experiment the reactor was opened and the reaction mixture was allowed to separate into clear phases. As the reaction proceeds the products accumulate in one or other of the phases according to their solubility.

Klepacova *et al*. (2005) studied etherification of glycerol with tert-butanol. The catalytic activity of Amberlyst 15 and two large-porous zeolites (H-Y and H-BEA) were compared. Dealkylation of di-ethers was not observed over zeolite catalysts. The maximum conversion of glycerol near 96% was reached at the temperature of 90ºC and at the molar ratio of tert-butanol / glycerol of 4:1 after 180 min. The most active catalysts for tert-butylation of glycerol at the used reaction condition were Amberlyst 15 and large-porous Zeolite H-BEA.

Klepacova *et al*. (2006) studied reaction of glycerol with tert-butyl alcohol in liquid phase on acid Amberlyst-type ion exchange resins (15, 35, 31 and 119). Amerlyst 15 and 35 are typical macroreticular ion-exchange resins and are commonly used as catalysts for the production of the aliphatic ether oxygenates used as gasoline (MTBE, ETBE, TAME). The optimal reaction temperature is 75 ºC and the glycerol conversion was 87.8% and 68.4% for A-35 and A-15 catalyst, respectively. The conversion of glycerol and the yield of ethers have increased with higher mole ratio of TBA/ Glycerol. It should be noted that feeding with stoichiometric mole ratio is insufficient. Etherification reaction of glycerol with isobutylene in nonaqueous conditions gives the highest yield of desired ethers. Water present in the reaction system has an inhibition effect on glycerol *tert*-butylation. The best results were reached when isobutylene was used as etherification agent (X_G = 100 %, Yield of di- and tri-ethers is 91.6 % for A-15 and 90.8 % for A-35). Etherification (*O*-alkylation) of glycerol is acid-catalysed reaction with formation of mono-, di-, tri-tert-butyl glycerol ethers. The formation of 1- and 1,3-ethers (primary –OH groups) is more probable against 2- and 1,2-ethers. Moreover, primary –OH groups of glycerol are preferred for tert-butylation due to the steric effect, too, because tert-butyl groups are voluminous.

Klepacova et al., (2007) studied the influence of catalyst, and temperature on the etherification of glycerol with isobutylene in the liquid phase catalyzed by strong acid ion-exchange resins of Amberlyst type (A-15 and A-35), *p*-toluenesulfonic acid and by two large-pore zeolites, H-Y and H-Beta. The highest glycerol conversion of 88.7% was achieved over zeolite H-Y after 8 h. Reaction over H-Beta zeolite runs faster with high selectivity to di-ethers, but formation of tri *tert*-butyl ethers of glycerol was sterically hindered. The highest amount of tri-ethers was observed over A-35. In the case of ion-exchange resins, A-35 gives about 10% higher initial rate than A-15. From the technological point of view the zeolites are not convenient as catalysts for studied reaction because of their easy deactivation and higher price to that of ion-exchange resins. The homogeneous catalyst (*p*- toluenesulfonic acid) provides better results in di-ethers formation. Mono-tert-butyl ether of glycerol is more polar and has a low solubility in diesel fuel and therefore the etherification of glycerol must be directed to the maximum yield of di- and tri-ethers.

Melero et al. (2008) investigated the etherification of glycerol with isobutylene over different sulfonic acid modified mesostructured silicas such as Propylsulfonic-acid-functionalized mesostructured silica (Pr- SBA-15) and Arenesulfonic-acid-functionalized mesostructured silica (Ar-SBA- 15). Sulfonic-acid-functionalized mesostructured silicas have demonstrated an excellent catalytic behavior in the etherification of glycerol with isobutylene to yield tert-butylated derivates. The products' selectivity were ordered as DTBG > TTBG > MTBG. Note that MTBG and DTBG can include several isomers depending upon the etherification position within the glycerol molecule. Hence, herein the terms MTBG and DTBG are intended to embrace all the possible mono- and di-tertbutyl- ethers, respectively. Reaction products detected by GC included glycerol ethers and in certain cases di-isobutylenes (DIB), coming from the acidcatalyzed dimerization of isobutylene, but TBA was not detected. The olefin dimerization is an undesired side reaction that depends upon the reaction conditions (especially favored at high temperatures and times when using over-stoichometric amounts of IB). The unique products coming from glycerol are tert-butylated derivates and poly-glycerols were not detected. Catalytic results are shown either in terms of absolute conversion of glycerol or in terms of weight products distributions or selectivities of glycerol toward tert-butylated derivates.

Likewise, in order to attain optimal glycerol conversion as well as high yields towards DTBG and TTBG is advantageous to work with moderate temperatures. Within the studied range, optimal conditions have been found to be 75 °C and isobutylene to glycerol molar ratio of 4:1. Using these reaction conditions, glycerol conversions up to 100% and combined selectivity towards di- and tri-tert-butylglycerol over 92% were achieved after 4 h of reaction over arenesulfonic-acid-modified SBA-15 without isobutylene oligomerization. The use of moderately strong acid centers, such as those located in arenesulfonic-acid-modified mesostructured silicas, provides improved results both in glycerol conversion and selectivity towards the desired products.

It is worthy to note that although the above literatures are mainly studied these ethers as diesel fuel additives; high octane numbers for the mixture of ethers has been reported (112-128(BRON) and 91-99(MBON)).

3.3 Etherification with entire FCC gasoline.

However, as shown in the literature, olefinic reactants are mostly limited as isobutene and isoamyleme.

These oxygenates can be produced from the etherification of olefin compounds with alcohol such as methanol and ethanol over a cation exchange resin catalyst such as Amberlyst 15 and Amberlyst 16 or acidic zeolite. In these studies, FCC gasoline is chosen as olefins. Oxygenates such as methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), tertiary amyl methyl ether (TAME) and tertiary amyl ethyl ether (TAEE) have been present interest.

Pescarollo et al. (1993) had investigated etherify FCC light gasoline with methanol. The higher ether can be produced from reaction between reactive olefins and methanol. The result showed olefins conversions are lower with larger atomic number of olefins. The conversion of isobutene is 84.2%, isopentene is 68.8% as closely approaches thermodynamic equilibrium.

Kiatkittipong et al. (2008) investigated the etherified FCC light gasoline with ethanol. The process of FCC light gasoline etherification with ethanol has several benefits. Firstly, the gasoline volume is effectively increased by adding ethers produced from ethanol which is renewable. Secondly, the etherified gasoline product has higher octane number with lower bRvp and amount of olefins content. The improvements in octane number and volume by reducing olefinicity and bRvp of the gasoline were reported.

Because not only a better catalytic catalytic activity for etherification, bust some isomerization also occurs without aromatization. Beta-zeolite was a more suitable catalyst than Amberlyst 16 for upgrading FCC gasoline with ethanol. Olefins and ethanol conversions increase with increasing ethanol ratio in feed. The cold start problem might not be occurred even in low bRvp as proven by satisfied drivability index (Kiatkittipong et al., 2009).

3.4 Simulation equilibrium of reaction.

Boyd et al. (1976) studied computation of multicomponent and multiphase equilibrium. The mixtures are computed by minimizing the gibbs free energy using fortran program but no use constrained form as minimizes using Powell's method. This program can applied to chemical and physical equilibrium and can handle up to three multicomponent phases, and 15 components.

Later, Mcdonald et al. (1885) examined the problem when the liquid phase is adequately moldeled by the Non-Random two liquid (NRTL) activity coefficient expressions and the vapor phase is assumed to be ideal. Limited research focused on etherification of FCC gasoline with alcohol. Andrzej et al. (1995) had been presented the thermodynamic analysis of the process of etherification of light FCC gasoline with methanol using the NDP FORTRAN-386. The assumptions of the chemical equilibrium are reached only for the reactions between methanol and C4-C7 olefins which having the double bond at a tertiary carbon atom were established. The reaction of isomerization of olefins and ethers was assumed to do not take place. Because of there are no thermodynamic data for C7 olefins and C6-C8 ethers. Two group contribution methods (Benson and Yoneda) were used to calculate the missing properties. The reaction in liquid phase was preferred. The equilibrium conversion in gas phase was lower due to phase reversion. Finally, the results from two group contribution method are corresponding.

Yhoothongkam (2008) studied the thermodynamic equilibrium of the etherification of FCC gasoline and ethanol by used a simulation program, Aspen plus version 11.1. The components of gasoline consist of C4-C7 hydrocarbons. The group contribution methods such as Ambore's method, Joback's method, Gani's method and Benson's method were applied to estimate the missing parameters (e.g. critical pressure, critical temperature, boiling point, standard Gibb's free energy of formation). The preliminary selection of group contribution method shows that Gani’s and Joback’s method are well-predicted for normal boiling point, critical temperature and critical pressure. Moreover Gani’s and Benson’s method showed good agreement with the properties from literatures for standard Gibb’s free energy of formation. Also, when applied the group contribution to Aspen plus simulator, Gani’s and Benson’s method yield the results close to those of experiments. However, Gani’s group contribution method cannot distinguish the properties of some components.

CHAPTER IV

RESEARCH PROCEDURE

The research procedure for the improvement of the fuel oil quality by the etherification of FCC gasoline with glycerol can be divided to two main part i.e. experimental and simulation.

4.1 Experimental section

4.1.1 Equipment and chemical

- Batch Reactor Apparatus

A cylindrical shape autoclave type reactor the volume of reactor was 100 cm^3 with reactor height of 8 cm and outside and inside diameters of 5 and 4 cm, respectively. The turbine was used to stir the mixture. A valve for liquid sampling and a port for the thermocouple were installed at the top. The mixture was stirred at the maximum speed of 1163 rpm in all the runs to minimize the external mass transfer resistance. At this speed, the effect of external mass transfer resistance could be neglected. The reactor was maintained at a constant temperature by circulating hot water in jackets. Figure 4.1 shows the batch reactor apparatus. The system was pressurized by N_2 at 2.6 MPa to ensure that all reaction components were in the liquid phase.

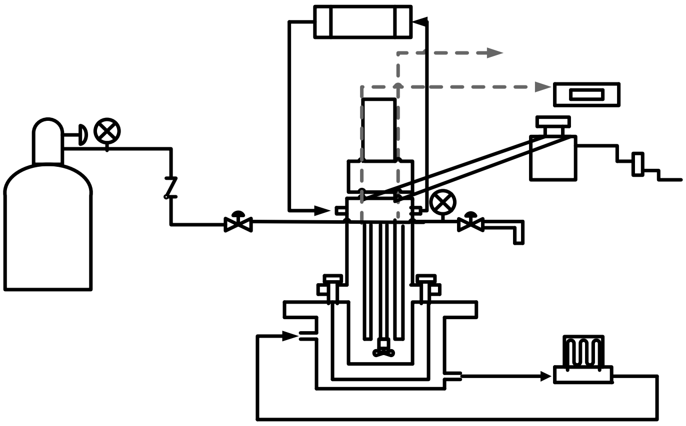


Figure 4.1 Batch Reactor Apparatus

- Chemicals

FCC gasoline is cut off from a catalytic cracking unit of Thai Oil Public Company. Glycerol grade AR (99.5 vol. %) from QRëC.

- Catalysts

Amberlyst 16, Amberlyst 15 and β-zeolite used in this study were purchased from Chemica Fluka and Tosoh (Japan), respectively. The catalysts were dried overnight in an oven at 110°C before use.

4.2 Experimental and sample analysis procedures

4.2.1 Experimental procedure

1. The reaction system consisted of FCC gasoline and glycerol with a volume ratio of 84:16 with 10 g of catalyst.

2. The solution was pressurized by N_2 gas to 2.6 MPa to prevent vaporization of liquid solutions and heated to the desired reaction temperature (343 K) for 10 h. and stirred at about 1163 rpm.

3. The samples of feed and product were collected at the initial and final of the experiment. It should be noted that for collecting the final product after run for 10 h, the reactor was cooled down to reach a room temperature before opening the reactor and collecting the sample in order to prevent the evaporation loss.

4. The effect of the amounts of catalyst was investigated by varied a catalyst weight for 0.5, 5 and 10 g.

4.2.2 Analysis

1. Chemical compositions analysis

In gasoline investigations, the compounds called “PIANO” which consisted of paraffins, isoparaffins, aromatics, naphthenes and olefins were determined with the amount of the oxygenates. The samples of feed and product were investigated by follows “PIANO” which was analyzed by the laboratory of Thai Oil Public Company Limited. In this analysis, the liquid samples were tested by using a gas chromatograph with SUPELCO capillary column as a separation column.

2. Fuel oil quality analysis

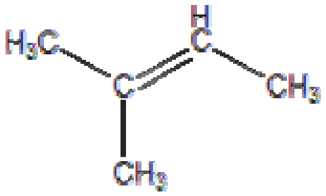
The standard analysis of Research Octane Number (RON), blending Reid vapor pressure (bRvp) and distillation temperature were carried out by follows the standard methods of following the standard methods of ASTM D -2699, ASTM D

5191-99 and ASTM D 86-05, respectively. All of analyses were tested by the laboratory of Thai Oil Public Company Limited and the laboratory of PTT. In addition, density was analyzed by using the pycnometer.

4.3 Simulation

4.3.1 Selection of approximate group contribution method

The various group contribution methods that will be applied to estimate the missing properties are Ambrose’s method, Joback’s method, Gani’s method and Benson’s method. The group contribution methods are divided in zero order, first order and second order. This research had been included all type of group contribution method. The first order group contribution method is the easiest of group contribution method. The procedure for use group contribution method will be described follow to; first, the specification of subgroup of component as you must draw the molecular structure before. But the second order group contribution method, the knowledge of stereochemistry must clearly understand about spatial structure. Alternatively, NIST web book allow you to upload or draw structure and then the detail of molecular structure will be showed, specially, when Benson’s method had been applied.



2-Methyl-but-2-ene

Figure 4.2 The molecular structure of 2-methyl-butene.

Table 4.1 The number of subgroup unit from difference method.

Subgroup type	Joback's	Gani's	Bensons's
First order group			
Alkyl carbon	-	-	-
>C<	-	-	-
>CH-	-	-	-
Double bond	-	-	-
CH3(1)	3	-	-
C=(3)	1	-	-
CH=(2)	1	-	-
CH3(1)	-	3	-
CH=C(3)	-	1	-
Second order group			
CH3-CHm=CHn m,n(0,2)	-	3	-
CH3-(=C)	-	-	3
=C-(2C)	-	-	1
=CH=(C)	-	-	1
Cis-	-	-	1
Optical isomer	--	-	1
Total symmetry	-	-	1

Table 4.2 The value of subgroup unit from difference method

Subgroup	Joback's			Gani's		
	Tc	Pc	Tb	Tc	Pc	Tb
Alkyl carbon	-	-	-	-	-	-
>C<	-	-	-	-	-	-
>CH-	-	-	-	-	-	-
Double bond	-	-	-	-	-	-
CH3(1)	0.0141	-0.0012	23.58	-	-	-
C=(3)	0.0117	0.0011	24.14	-	-	-
CH=(2)	0.0129	-0.0006	24.96	-	-	-
CH3(1)	-	-	-	1.6781	0.0199	0.8894
CH=C(3)	-	-	-	8.9582	0.0126	1.7957
CH3-CHm=CHn m,n(0,2)	-	-	-	0.0167	-0.00018	0.0668

Second, identify the value of each subgroup; take the value from handbook such as Bruce E. Poling et al. or from literature. In this research, the example for 2-methyl-2-butene is shown in Table 4.3 and Table 4.4.

Table 4.3 The value of subgroup unit from difference method of 2-methyl-2-butene

Subgroup type	Joback's	Gani's	Bensons's
First order group			
CH3(1)	-43.96	-	-
C=(3)	92.36	-	-
CH=(2)	48.53	-	-
CH3(1)	-	-8.030	-
CH=C(3)	-	93.745	-
Second order group			
CH3-CHm=CHn m,n(0,2)	-	0.95	-
CH3-(=C)	-	-	-
=C-(2C)	-	-	-
=CH=(C)	-	-	-
Cis-	-	-	-
Optical isomer	--	-	-
Total symmetry	-	-	-

Table 4.4 The value of subgroup unit from Benson's method of 2-methyl-2-butene.

Subgroup	Benson's	
	Second order group	
	ΔH_f (kJ/mol)	S^o (J/mol K)
CH3-(=C)	-42.19	127.29
=C-(2C)	43.28	-53.16
=CH-(C)	35.96	33.36
Cis-	4.19	-
C	0	6
H_2	0	130

Finally, substitute in equation of each group contribution method. The examples for calculation of properties are showed below;

Normal boiling point;

Joback's

$$T_b = 198 + \sum_k N_k (tbk)$$

$$\sum_k N_k (tbk) = (3*23.58) + (1*24.14) + (1*24.96) = 119.94$$

T_b =317.94K

Critical temperature;

Gani's

$$Tc(K) = 181.128\ln[\sum_k N_k(tck) + W\sum_j M_j(tc2j)]$$

Tc (K) =181.128ln [(3*1.6781) + (1*8.9582) + (3*0.0167)]

Tc = 400K

Critical pressure;

Joback's

$$P_c(bar) = [0.113 + 0.0032N_{atoms} - \sum_k N_k(pck)]^{-2}$$

Pc= {0.113+ (0.0032*15)-[(3*(-0.0012)) + (1*0.0011) + (1*(-0.0006))]}$^{-2}$

Pc = 37 bar

Gibbs free energy of formation

Benson's

$$\Delta H_f^o(298.15K) = \sum_k N_k(\Delta H_{fk}^o)$$

$\Delta H_f^o(298.15K) =$ [(3*(-42.19)) + (1*43.28) + (1*35.96) + (1*4.19)] = -43.14 kJ/mol

$$S_s^o = R\ln(N_{oi}) - R\ln(N_{ts})$$

$S_s^o =$ 8.314*[0] = 0 J/ mol K

$S_{el}^o(298.15K) = \sum_e v_e(S_e^o) =$ [(5*6) + (10*130*0.5)] = 680 J/ mol K.

$$S^o(298.15K) = \sum_k N_k(S_k^o + S_s^o) + S_s^o$$

$S^o(298.15K) =${(3*127.29) + (1*-53.16) + (1*33.36)} = 362 J/mol K

= 0.362 kJ/mol K.

$$\Delta G_f^o(298.15K) = \Delta H_f^o(298.15K) - 298.15[S^o(298.15K) - S_{el}^o(298.15K)]$$

$\Delta G_f^o(298.15K) =$ -43.14-298.15[0.362-0.68] = 51.57 kJ/mol

4.3.2 Simulation Program

The various flexibility and powerful of Aspen program can be applied to investigate the simulation of several reactions. The reactions of FCC light gasoline are applied in this program. Due to the components are not appearing in Aspen plus data bank so the new components must be specified and added to

Aspen plus program. The Aspen plus program allow user to add the functional group for each component include the method of group contribution. Various group contribution methods are applied to this research such as Benson’s method, Joback’s method and Gani’s method. The details of specification of new components in Aspen plus Program are shown in Appendix D. In this research the Chemdraw program was applied to create the new molecular structure. The type of file from Chemdraw program must be mole file (.mol). The functional groups of each component of several methods are listed in Appendix A to C. The properties of components that estimated by Aspen plus program will be brought to compare with the data from handbook.

CHAPTER V

RESULTS AND DISCUSSION

5.1 Etherification of FCC gasoline with glycerol

Table5.1 Composition of original FCC gasoline in volume percent

Carbon number	n-Paraffins	i-Paraffins	Olefins	Naphtenes	Aromatics	Total
C4	0.215	0.111	1.208	0.000	0.000	1.534
C5	0.996	7.691	6.693	0.000	0.000	15.380
C6	1.102	11.764	7.053	1.631	0.323	21.874
C7	0.794	7.146	7.246	2.564	2.230	19.980
C8	1.059	5.953	0.688	2.230	4.608	14.538
C9	0.391	3.030	1.937	2.827	5.079	14.264
C10	0.257	2.620	0.000	0.137	5.563	8.577
C11	0.281	0.829	0.000	0.087	0.766	1.864
C12	0.077	0.446	0.000	0.205	0.909	1.637
Total	5.072	39.591	24.825	9.681	20.478	99.647

The compositions of original FCC gasoline are shown in Table 5.1. Most olefins were in the range of C_5-C_7 hydrocarbons. The fraction of total olefins was about 25 vol%.

5.1.1 Catalyst screening

The catalyst screening experiments were carried out at the following condition; i.e. catalyst weight = 10 g, *T* = 343 K, *P* = 2.6 MPa and the volume ratio of FCC gasoline to glycerol = 84:16. Three catalysts i.e. Amberlyst 16, Amberlyst 15 and Beta-zeolite were investigated. The physical properties of catalysts were shown in Table 5.2.

Table 5.2 Physical properties of catalysts

	Structure	Crosslinking degree (%)	Pore diameter (nm)	Particle size (μm)	Surface area (m^2/g)	Pore volume (cm^2/g)
Amberlyst 16	macroporous	12	20	700	45	1.82
Amberlyst 15	macroporous	20	30	600-850	53	0.40
Beta-zeolite	microporous aluminosilicate	-	0.58	45	625	0.129

(a) (b)

Figure 5.1 Mixture of glycerol and FCC gasoline (a) before reaction and (b) after 10 h reaction time in case of incomplete conversion of glycerol.

It should be noted that because of phase separation, no samples were taken during the experiment, since it could not be guaranteed that the sample would well represent the reaction mixture and its phases (Karinen et al., 2006). Figure 5.1 (a) represents two phases separation between glycerol and FCC gasoline before the reaction since glycerol and FCC gasoline are insoluble in each other. Fig. 5.1 (b) shows the mixture after 10 h reaction time in case of incomplete conversion of glycerol. As the reaction proceeds the products accumulate in one or other of the phases according to their solubility. Upper phase has non-polar phase such as hydrocarbons, di-ethers and tri-ether. Lower phase has polar phase such as glycerol and mono-ethers. However, that all components were present in some degree in both phases. The concentration of products and reactants was changing during the reaction. At some stage of the reaction, the two phases dissolve in each other and only one phase remained (Karinen and Krause, 2006). However, in our study the gasoline etherified products are tested for several gasoline properties (e.g. RON, bRvp). The existing of glycerol in gasoline might be harmful for the testing instrument, therefore the reaction condition which can convert glycerol completely is required.

The activity of glycerol was higher than that of methanol or ethanol as a result of the increase of dielectric constant or polarity. The value of dielectric constants decreased with increasing of molecular weights of alcohols which were 42.5, 32.6 and 24.3 for glycerol, methanol and ethanol, respectively. The more polar component could be preferably adsorbed over the actives sites than the less polar component (Karinen et al., 2001). It has been claimed that a certain polarity is demanded to swell the pores of ion exchange resin catalytic site (Karinen et al., 2001). Amberlyst 15 and 16 are typical macroreticular ion exchange resins and are commonly used as catalysts for production of ethers oxygenates to gasoline (MTBE, ETBE, TAME). The characteristics of two strong acid macroeticular ion exchange resins and Beta-zeolite were shown in Table 5.2. The degree of crosslinking has a direct effect on the ion exchange resin swelling; when there is an increase of the crosslinking rate, the structure becomes more rigid (Rodriguez et al., 1975). Among three catalysts, only Amberlyst 16 gives a complete conversion of glycerol after 10 hours of reaction. Therefore Amberlyst 16 was selected as a suitable catalyst for the reaction.

5.1.2 The influence of the amount of catalyst

The influence of the amount of catalyst experiments were carried out at the following condition; i.e. catalyst weight = 0.5, 5, 10 g of Amberlyst 16, T = 343 K, P = 2.6 MPa and the ratio of FCC gasoline to glycerol = 84:16. With Amberlyst 16 less than 10 g, glycerol could not be converted completely.

5.1.3 Effect of operating temperature

The effect operating temperature experiments were carried at temperature of 323, 333 and 343 K. Glycerol conversion increased with increasing operating temperature from 323 K to 343 K. It should be noted that glycerol could be completely converted within 10 hours with the operating temperature of 343 K.

Figure 5.2 shows a comparison of C4-C7 iso-olefins between FCC gasoline and FCC etherified with glycerol. Iso-olefins are reactive olefin for etherification, small iso-olefins i.e. C_4 –C_6 iso-olefins decrease after etherification reaction, however, larger atomic number of iso-olefins i.e. C_7 iso-olefins are similar or slightly increase.

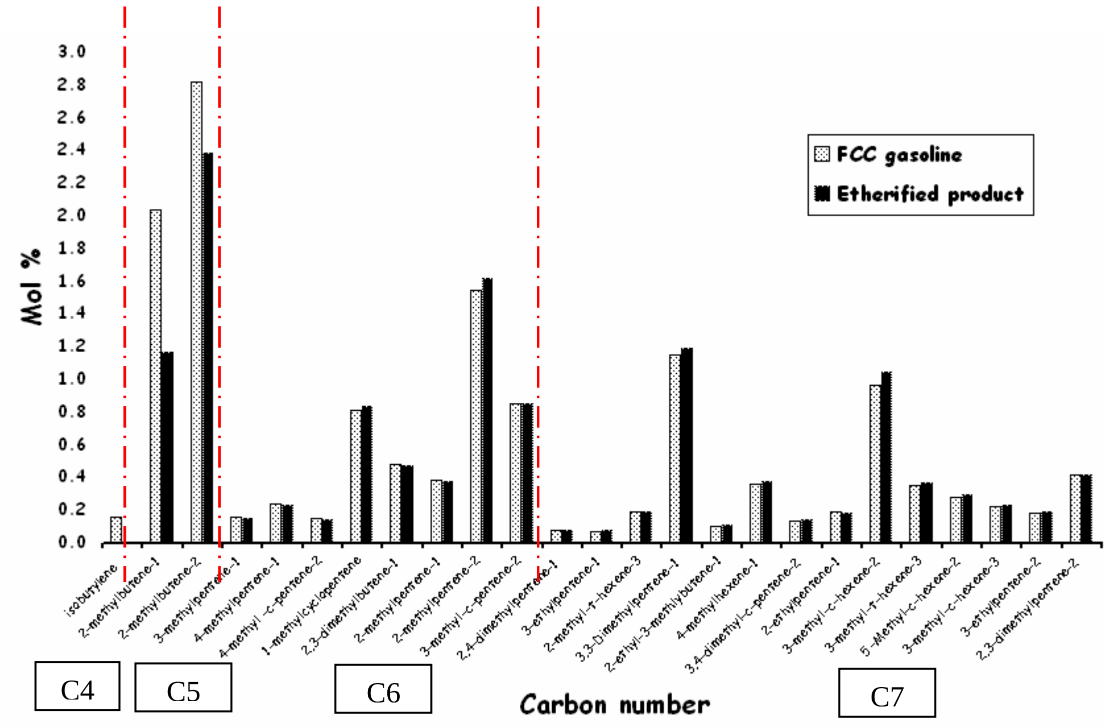


Figure5.2 Comparison of C4-C7 iso-olefins reduction between FCC gasoline and FCC etherified with glycerol

It is worthy to note that olefins conversions are lower with larger atomic number of olefins because large molecular of olefins hardly entries to pores of catalyst (Hu et. al. 2006). The tendency of these results was similar to that of the etherified FCC gasoline with methanol and ethanol experimented by Pescarollo et al. (1993) and Kiatkittipong et al. (2008; 2009), respectively.

5.2 Characterization of etherification products and FCC gasoline

Research Octane number (RON) and blending Reid vapor pressure (bRvp) of etherification products analyzed were shown in Table 5.3. The results show that RON of etherified FCC gasoline is higher than that of original FCC gasoline. It should be note that very limited work reported the octane number of the ethers derived from glycerol. Octane numbers for the mixture of ethers from IA and glycerol are in rage of 112-128 (BRON) and 91-99 (BMON) (Wessendorf et al., 1995). This implies that the RON of others ethers product might be higher than that of olefinic compounds which were consumed in the reaction. The bRvp of etherified FCC decrease form 6.5 psia to 4.5 psia. The reduction of bRvp is beneficial especially for hot countries or in summer. It should be noted that the increase of RON in case of etherified with glycerol are different from ethanol. In our previous study Kiatkittipong et at. (2008), studied etherification of FCC gasoline was etherified with ethanol (80:20 vol%) catalyzed by β-zeolite and RON of 94.1 could be obtained. Since the unreacted ethanol can be left in the gasoline therefore the RON of the etherified product also influenced by ethanol which have high octane ($RON_{ethanol}$ = 118). However, in the case of glycerol, glycerol could not be remaining in the gasoline. Therefore, the RON improvement might be only due to the etherification with glycerol. On the contrary, the bRvp of etherified FCC with glycerol are lower than that of etherified with 20 % vol ethanol. This is due to high bRvp of ethanol remaining in the gasoline.

Table 5.3 Comparison of gasoline properties

	FCC gasoline	Etherified FCC gasoline with glycerol
RON	88	90.1
bRvp (psia)	6.5	4.5
Drivability index, DI °C (°F)	631(1168)	636.45(1177.61)
Estimated minimum cold start temperature°C (°F)	-5.63(21.87)	1.94(35.49)
Density (g/cm^3)	0.7186	0.7403

Drivability index provides the relationship between drivability and distillation properties. Drivability index is key motor gasoline specification in the US. The distillation temperature represents the volatility property of gasoline, T10 represents the gasoline ability to vaporize rapidly and enable cold starting, and T50 and T90 represent the heavier gasoline components' ability to vaporize as the engine warms up and are burnt during combustion. The fuel parameters that influence cold weather drivability are not simple and can vary widely from one vehicle to another. An overall drivability index (DI) has been developed in the U.S. where:

$$DI = (0.5\times T10) + T50 + (0.5\times T90) \tag{5.1}$$

Where T10 = temperature (°F) at which 10% of the fuel is vaporized

T50 = temperature (°F) at which 50% of the fuel is vaporized

T90 = temperature (°F) at which 90% of the fuel is vaporized

This equation has been developed and refined, and a later version for use in the U.S. is as follow [French et al. (2005), Magyar et al. (2005), and Conocophillips.]:

$$DI = (1.5\times T10) + (3\times T50) + T90 \quad (5.2)$$

When oxygenate are present in the gasoline, the DI could be corrected as follows [Lippa et al. (2006)]

$$DI = (1.5\times T10) + (3\times T50) + T90 + 20 \times (\text{wt\% oxygen}) \quad (5.3)$$

In order to minimize evaporative emissions can lead to poor cold weather drivability. Poor vaporization leans the vapor air-to-fuel ratio in the combustion chamber and leads to loss of engine power and roughness, and increases engine hydrocarbon emissions. The DI maximum allowed at the refinery gate will vary seasonally, up to the 1250 maximum that would be allowed in areas that have hot summers. However, the values of DI of gasoline products are in the satisfied range of the gasoline specification.

The minimum cold start temperature could be estimated by the empirical relation as (Lippa et al. (2006))

$$\text{Minimum cold start temperature } (^\circ C) = (5.62\times (\sqrt{T10}-40))-30 \quad (5.4)$$

As shown in Table5.3, the estimated minimum cold start temperature and drivability index, DI of FCC gasoline and etherified gasoline. However, the appropriate values of DI and minimum cold start temperature strongly depend on the regional and seasonal of their used. Figure 5.3 shows distillation curve of FCC gasoline, etherified FCC gasoline with glycerol or ethanol increase initial boiling point (IBP) from original FCC gasoline. The results might support the decreasing of the bRvp of etherified product as previously shown in Table 5.3 and previous study (Kiatkittipong et al., 2008). Etherified FCC gasoline with glycerol showed higher distillation temperature in all volume percents evaporated than that of original FCC gasoline.

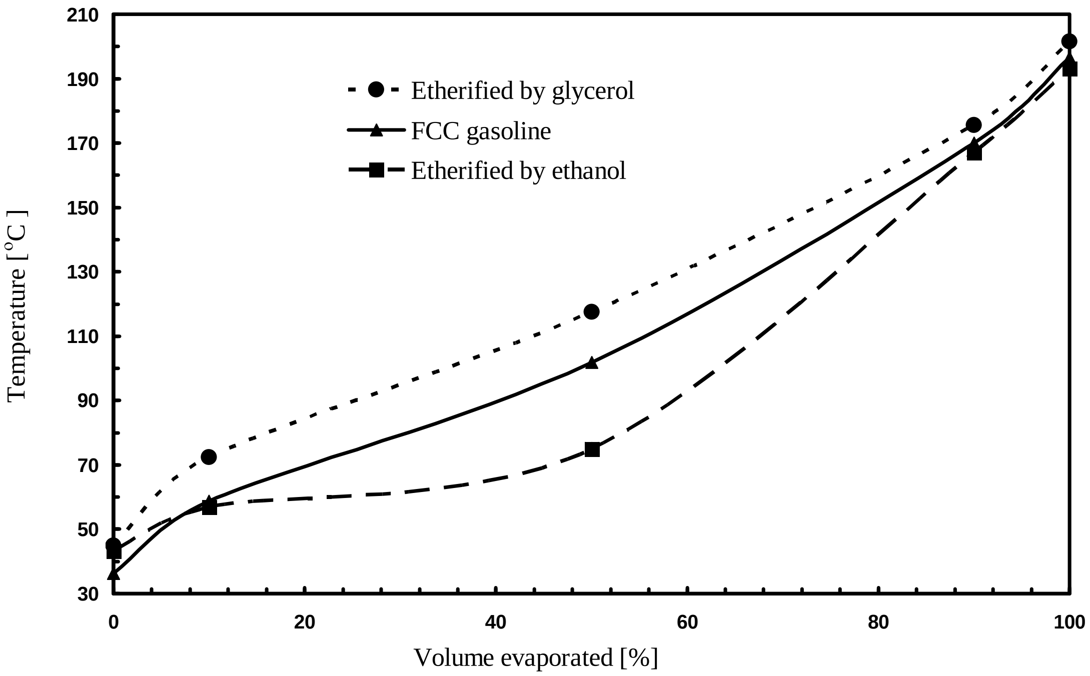


Figure5.3 Distillation curve from D-86 Tests

5.3 Group Contribution

This section will be compared various group contribution methods: Joback's method, Gani's method and Benson's method. The group contribution methods can be applied to calculate the critical temperature, critical pressure, normal boiling point and Gibbs free energy of formation. Then the subgroup from different group contribution methods will be added to Aspen plus simulator to create the thermodynamic databank of unavailable component in Aspen Plus.

This shows the reaction products of glycerol with FCC gasoline.

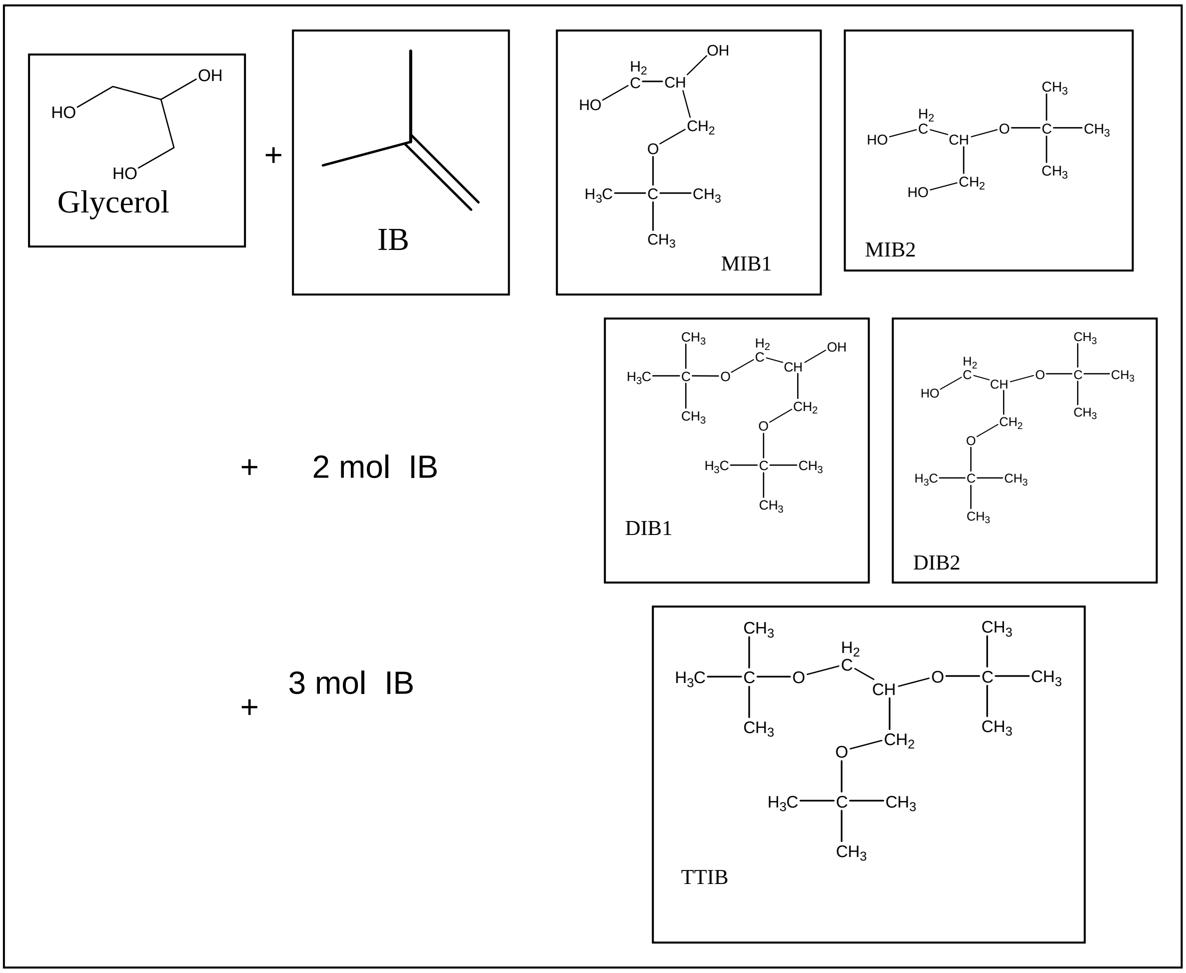


Figure5.4 Reaction products of glycerol with isobutylene

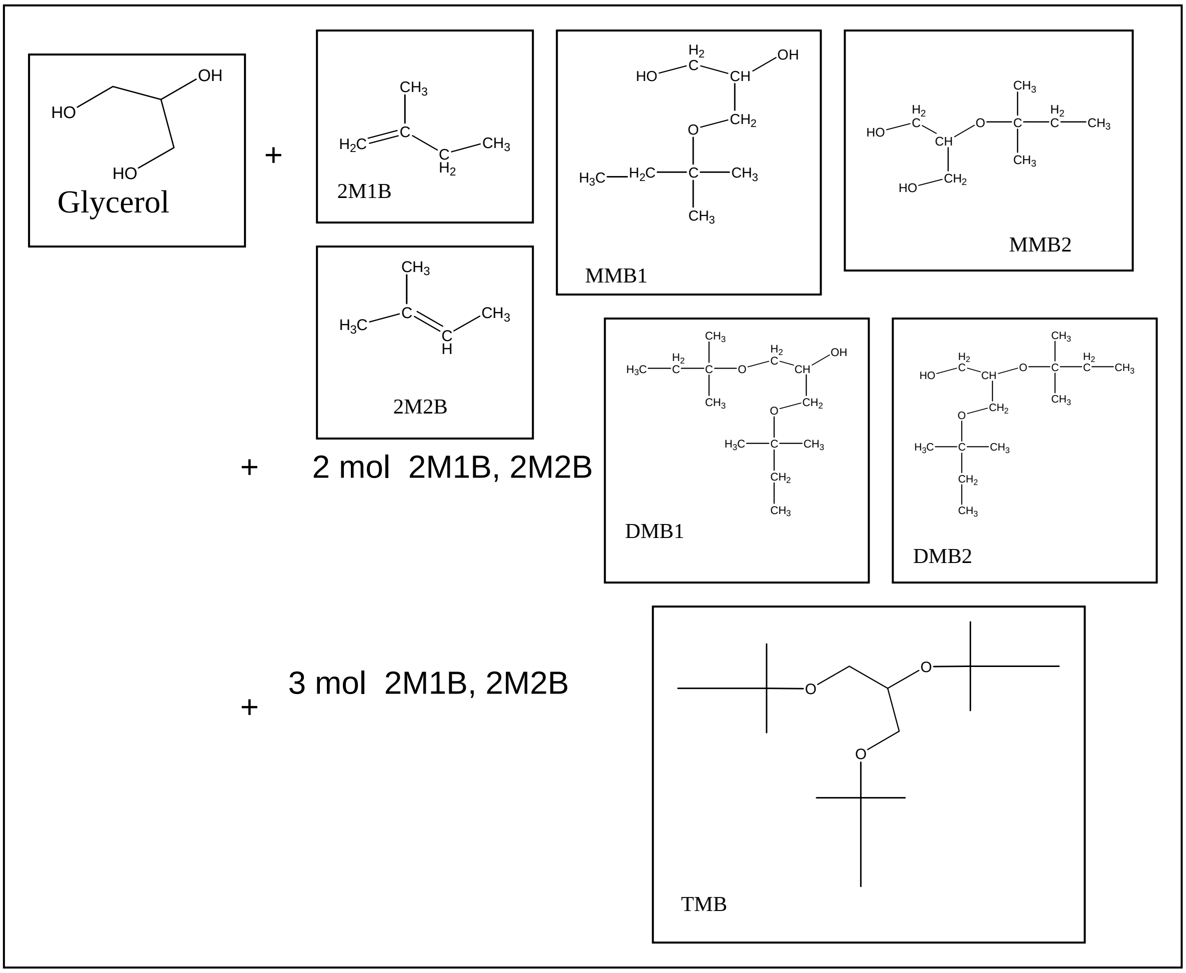


Figure5.5 Reaction products of glycerol with 2-methyl-1-butene and 2-methyl-2-butene

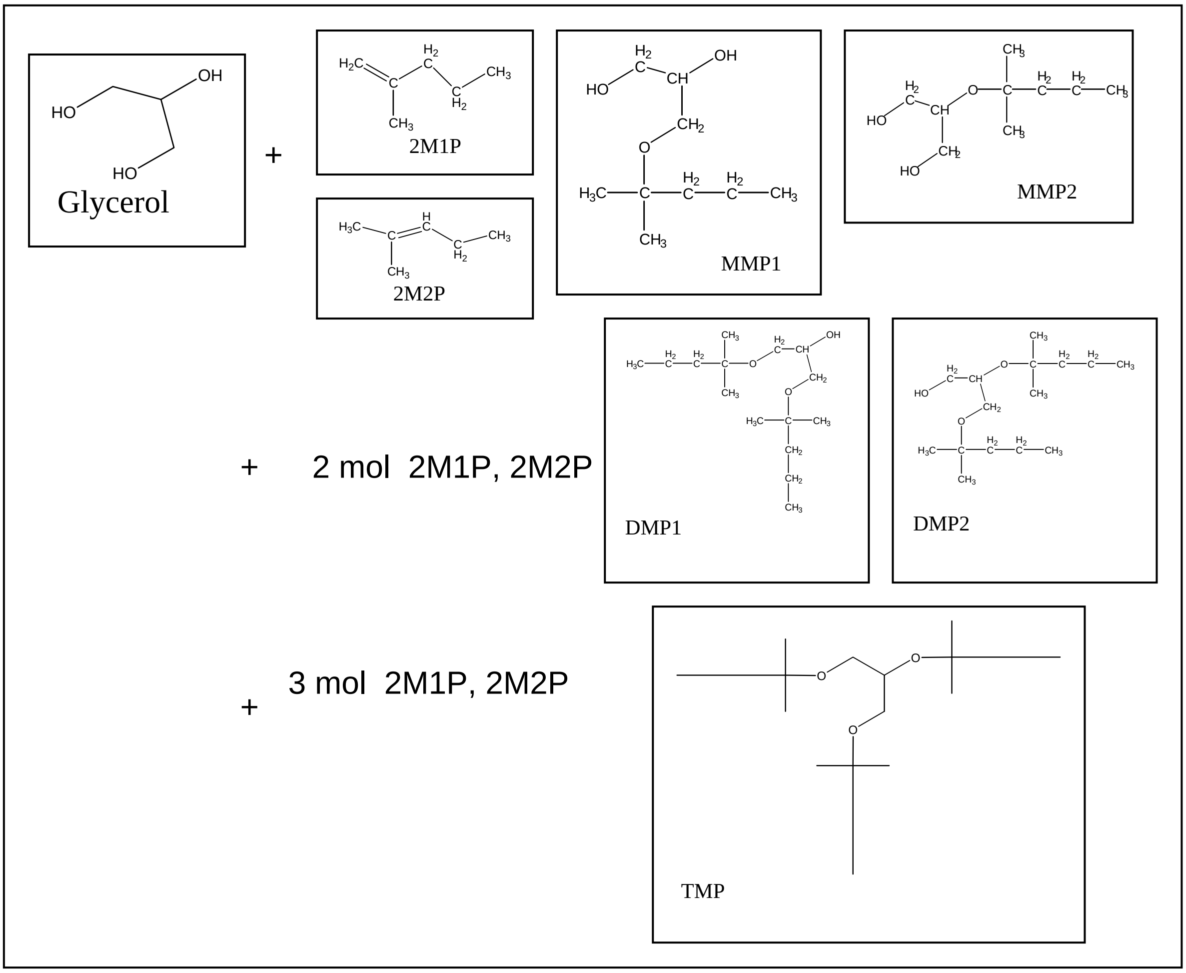


Figure5.6 Reaction products of glycerol with 2-methyl-1-pentene and 2-methyl-2-pentene

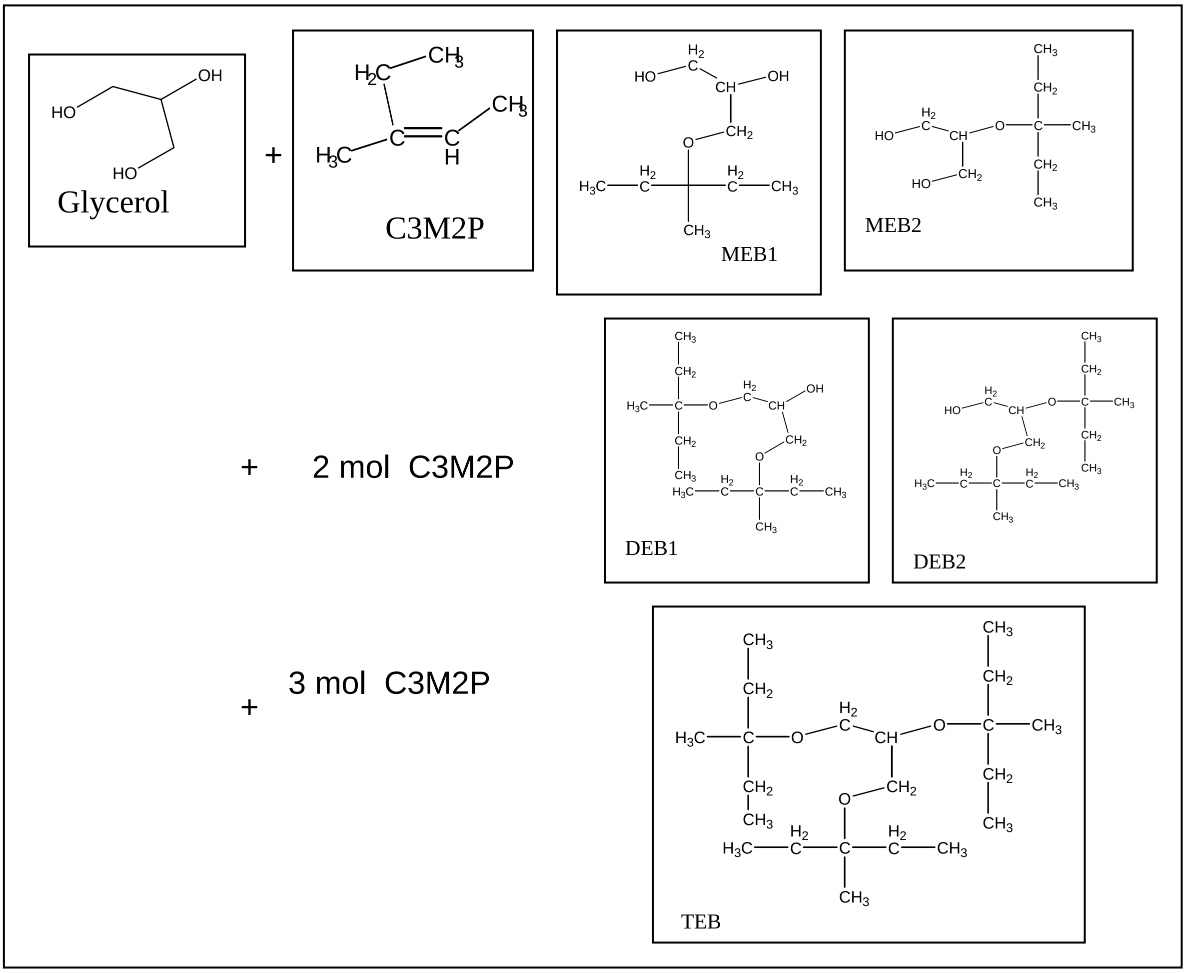


Figure5.7 Reaction products of glycerol with cis-3-methyl-2-pentene

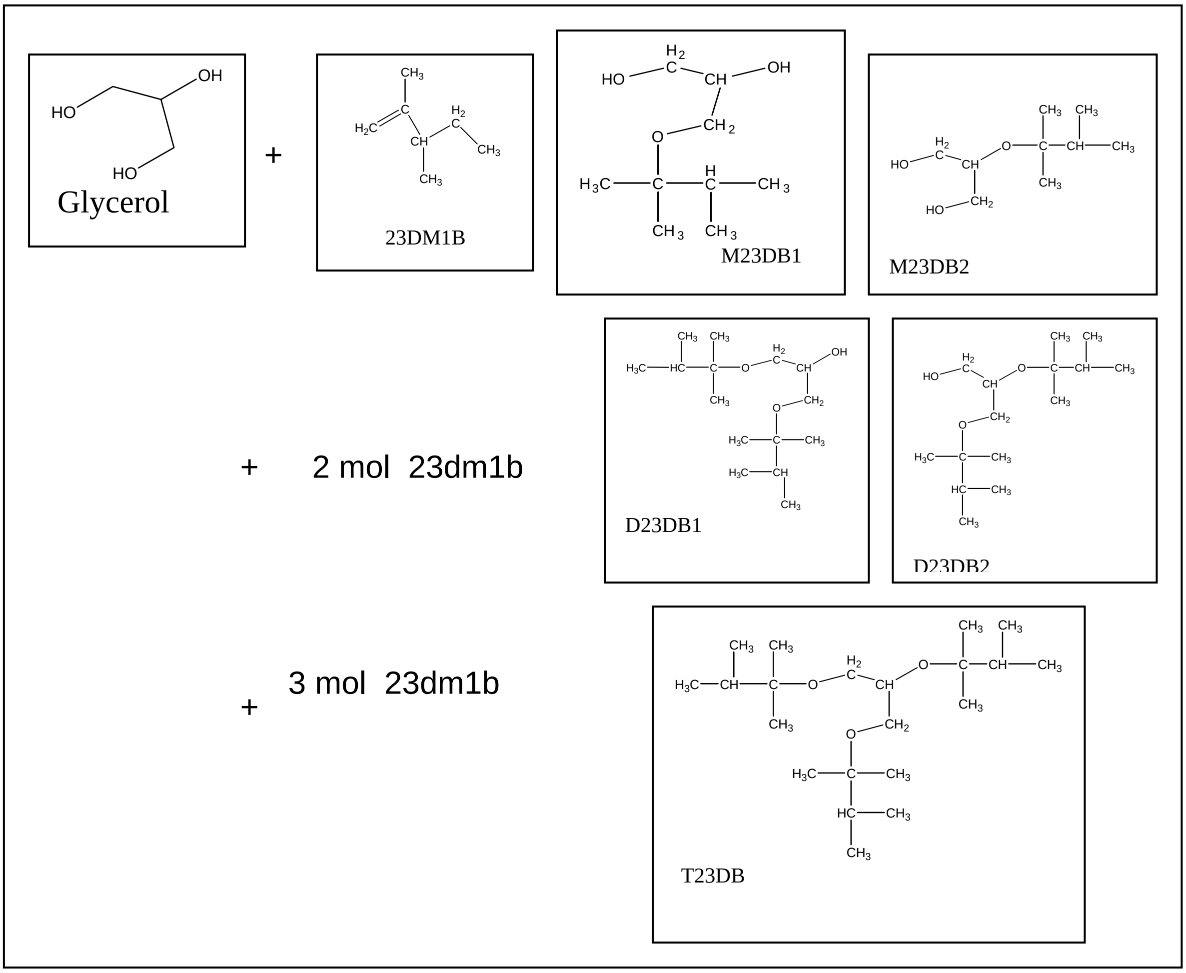


Figure5.8 Reaction products of glycerol with 2,3-dimethyl-1-butene

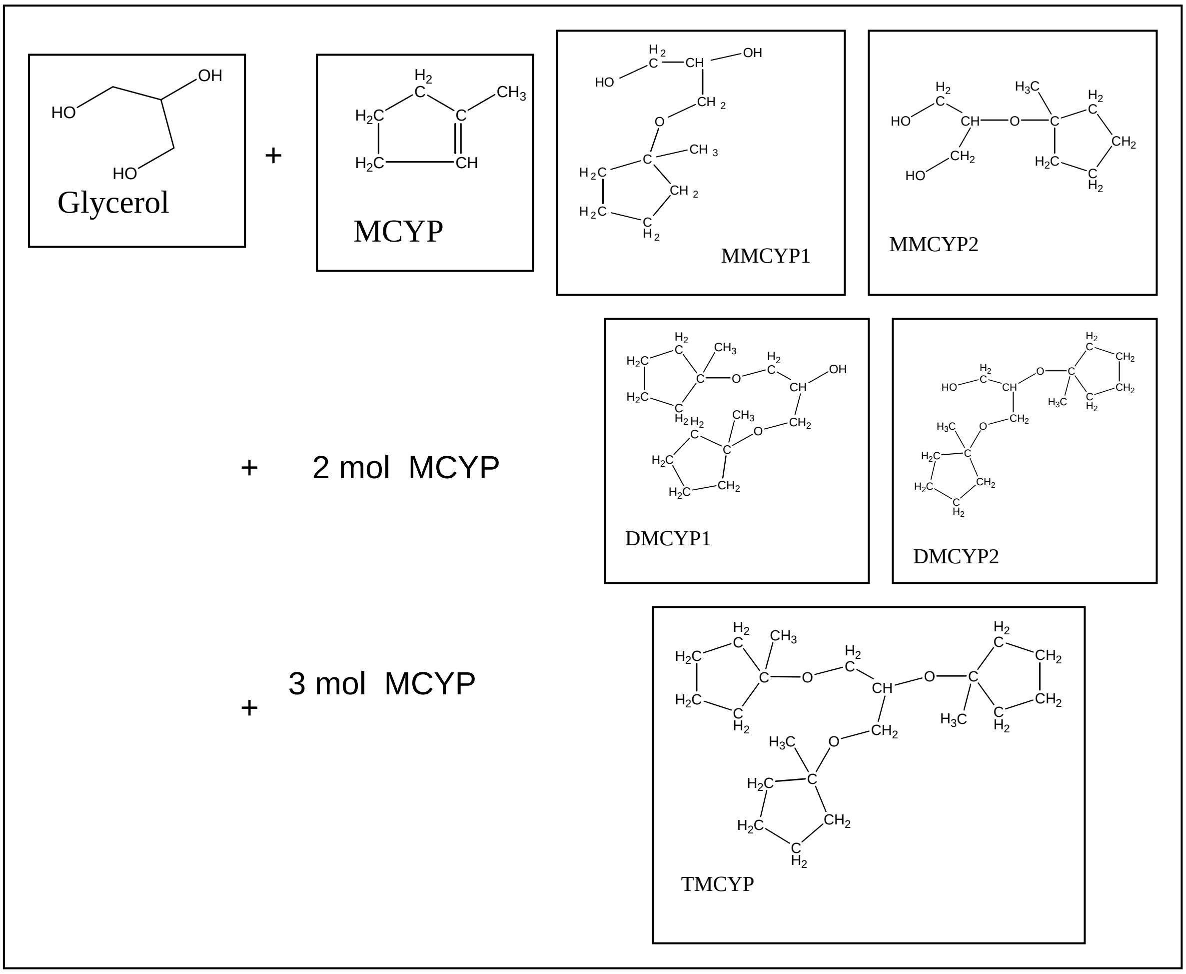


Figure5.9 Reaction products of glycerol with 1-methylcyclopentene

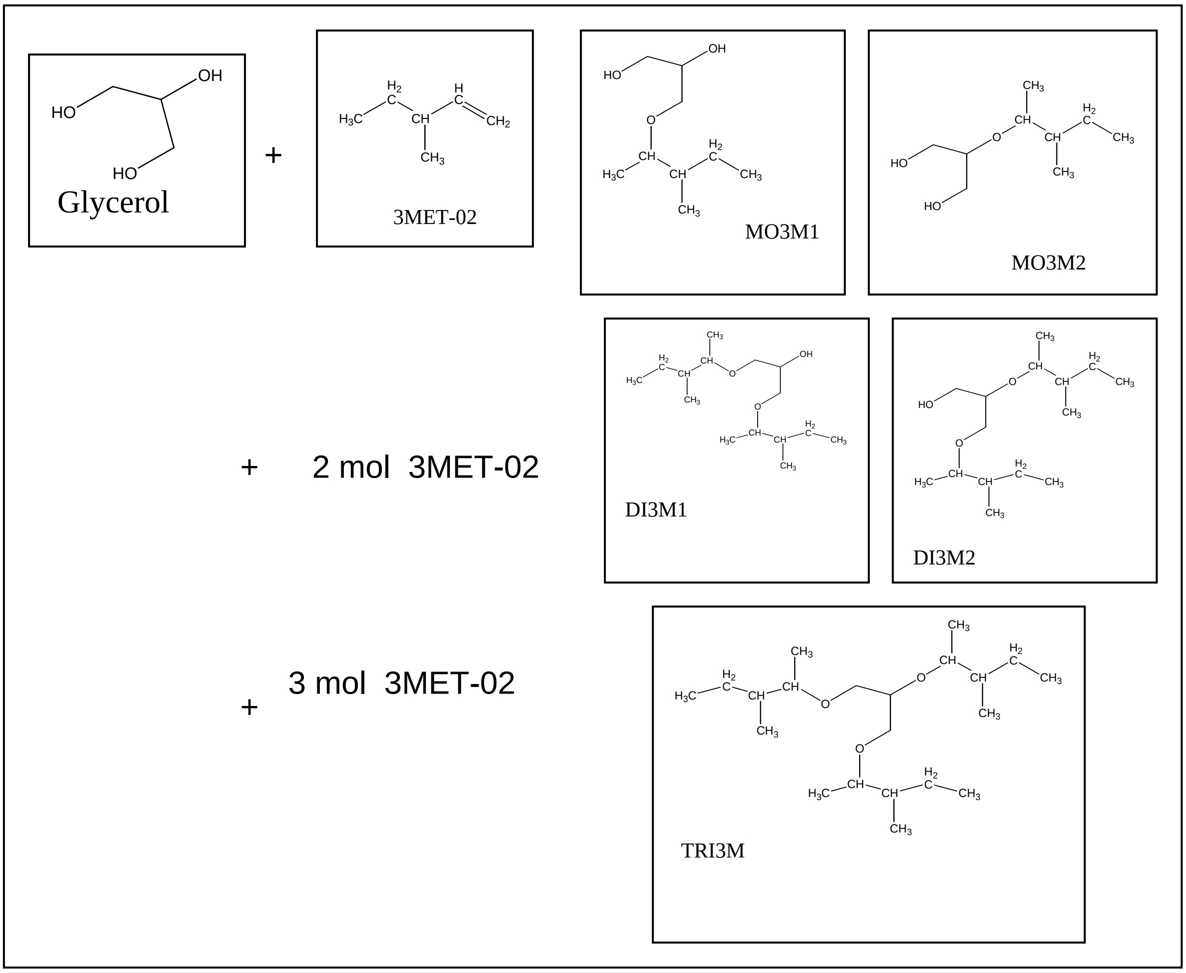


Figure5.10 Reaction products of glycerol with 3-methyl-1-pentene

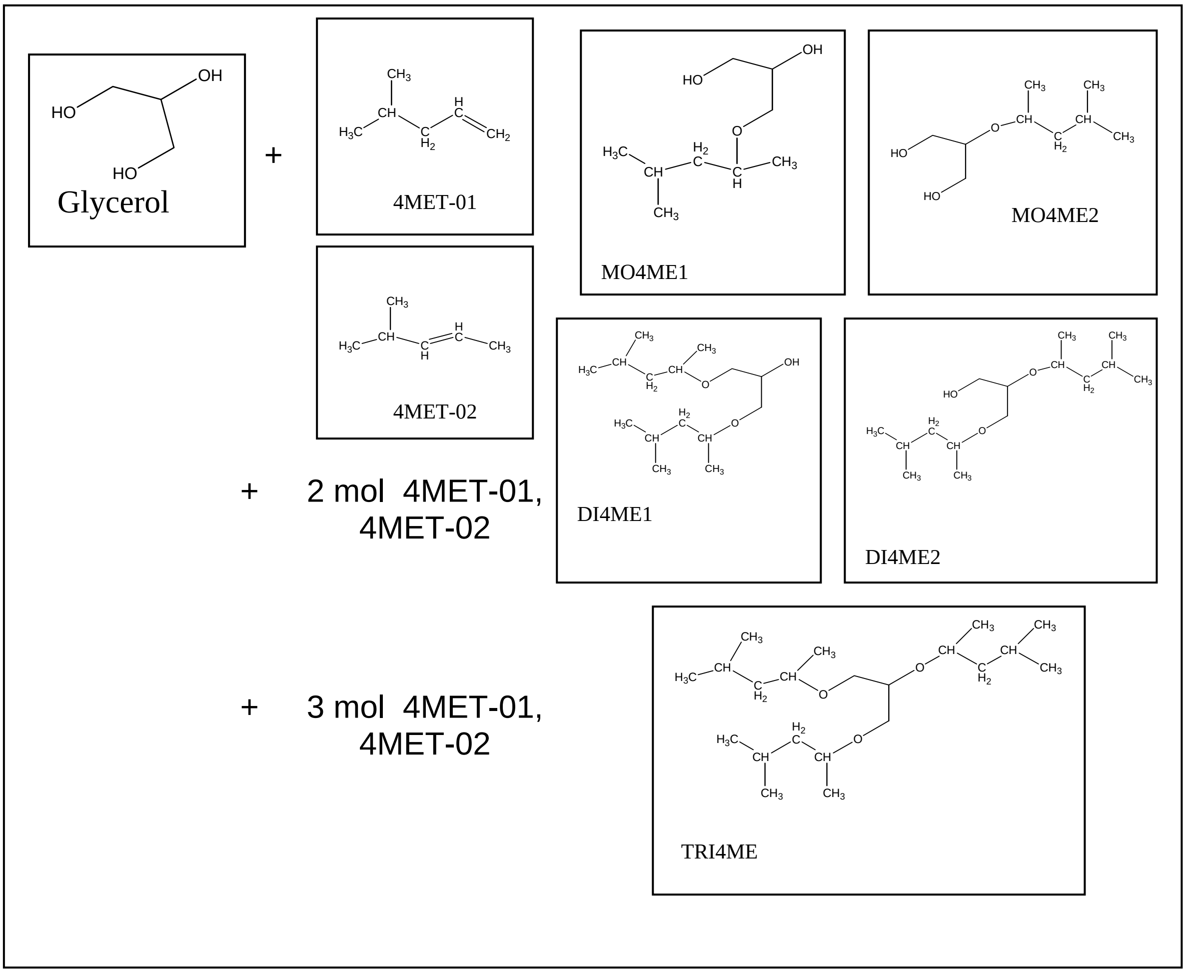


Figure5.11 Reaction products of glycerol with cis-4-methyl-2-pentene and 4-methyl-1-pentene

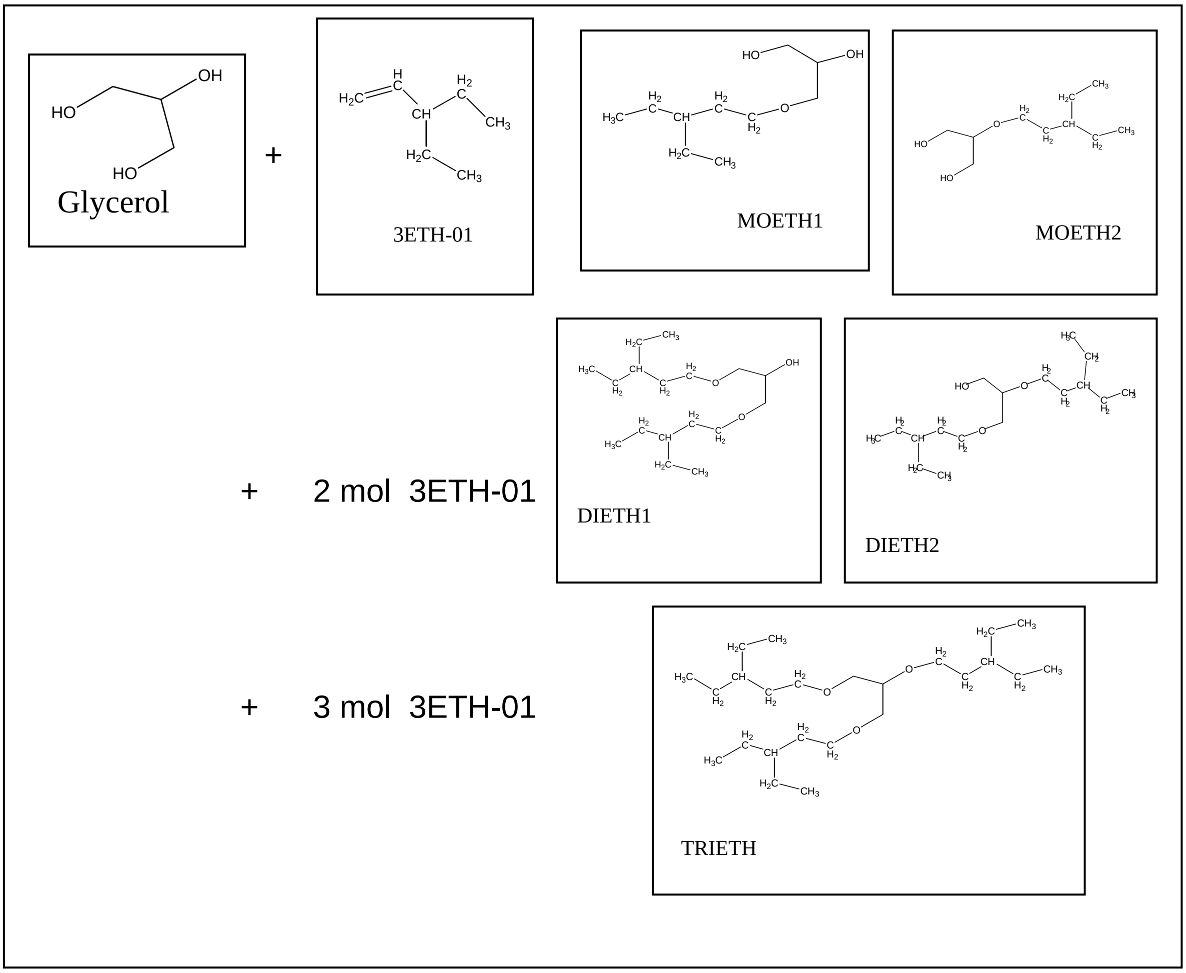


Figure5.12 Reaction products of glycerol with 3-ethyl-1-pentene

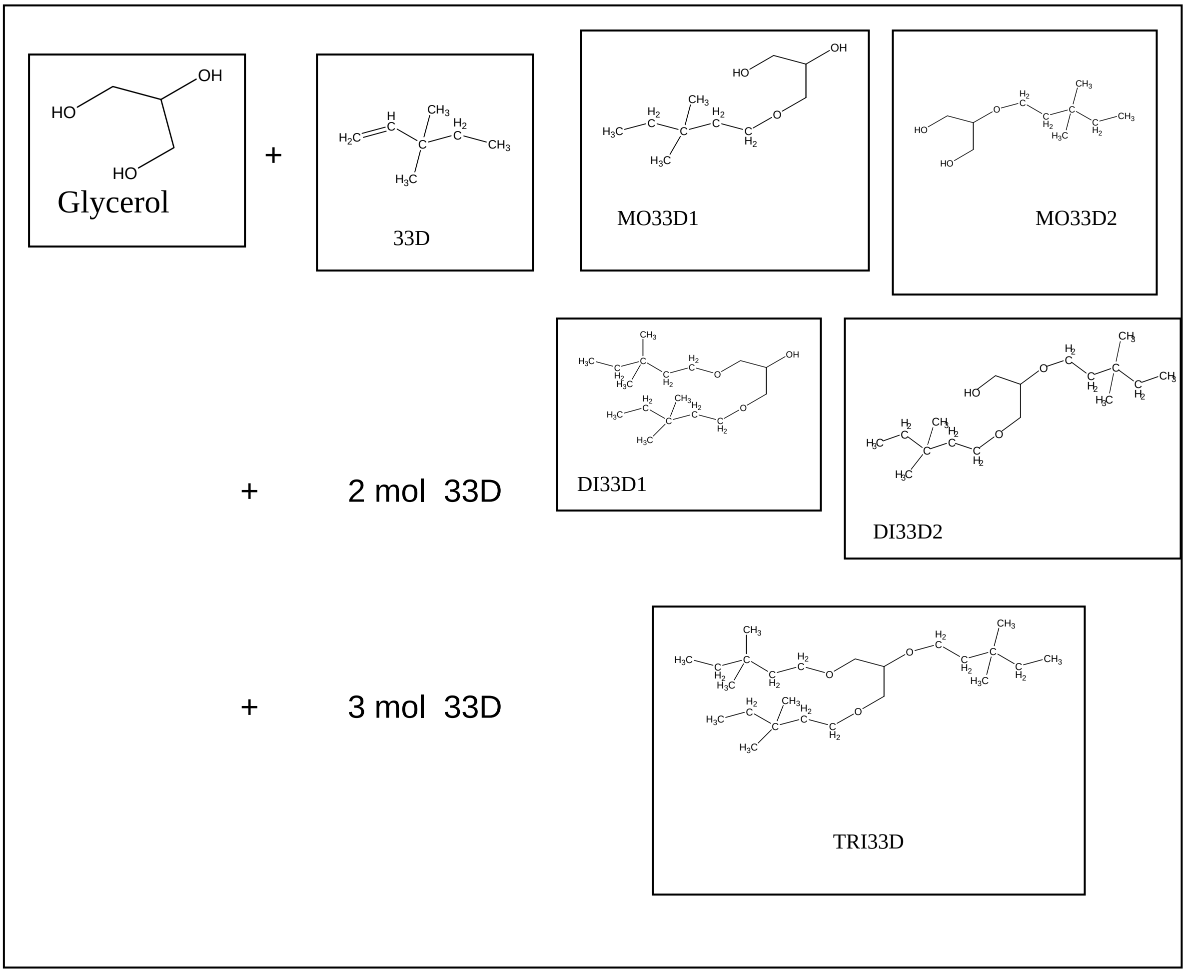


Figure5.13 Reaction products of glycerol with 3,3-dimethyl-1-pentene

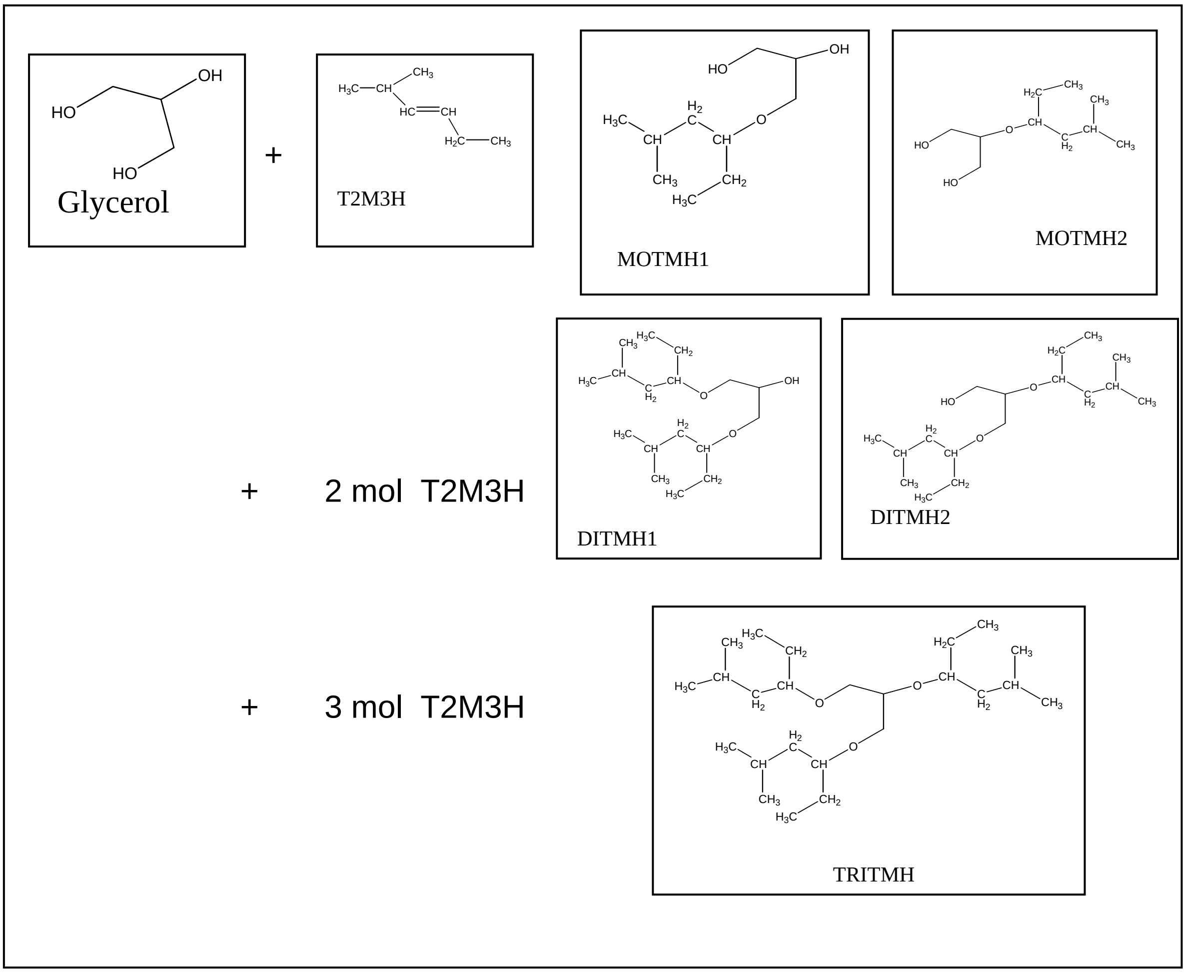


Figure5.14 Reaction products of glycerol with tran-2-methyl-3-hexene

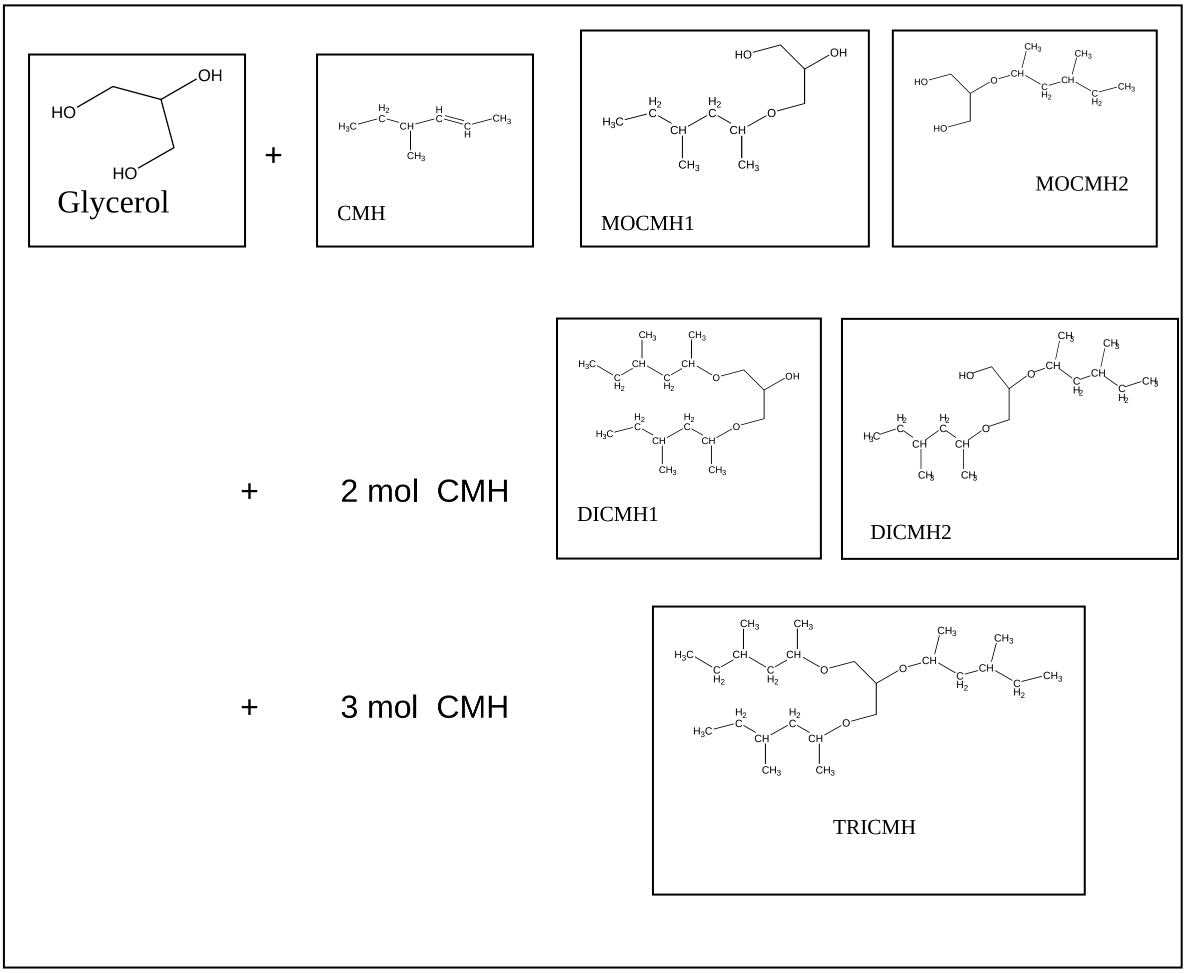


Figure5.15 Reaction products of glycerol with cis-5-methyl-2-hexene

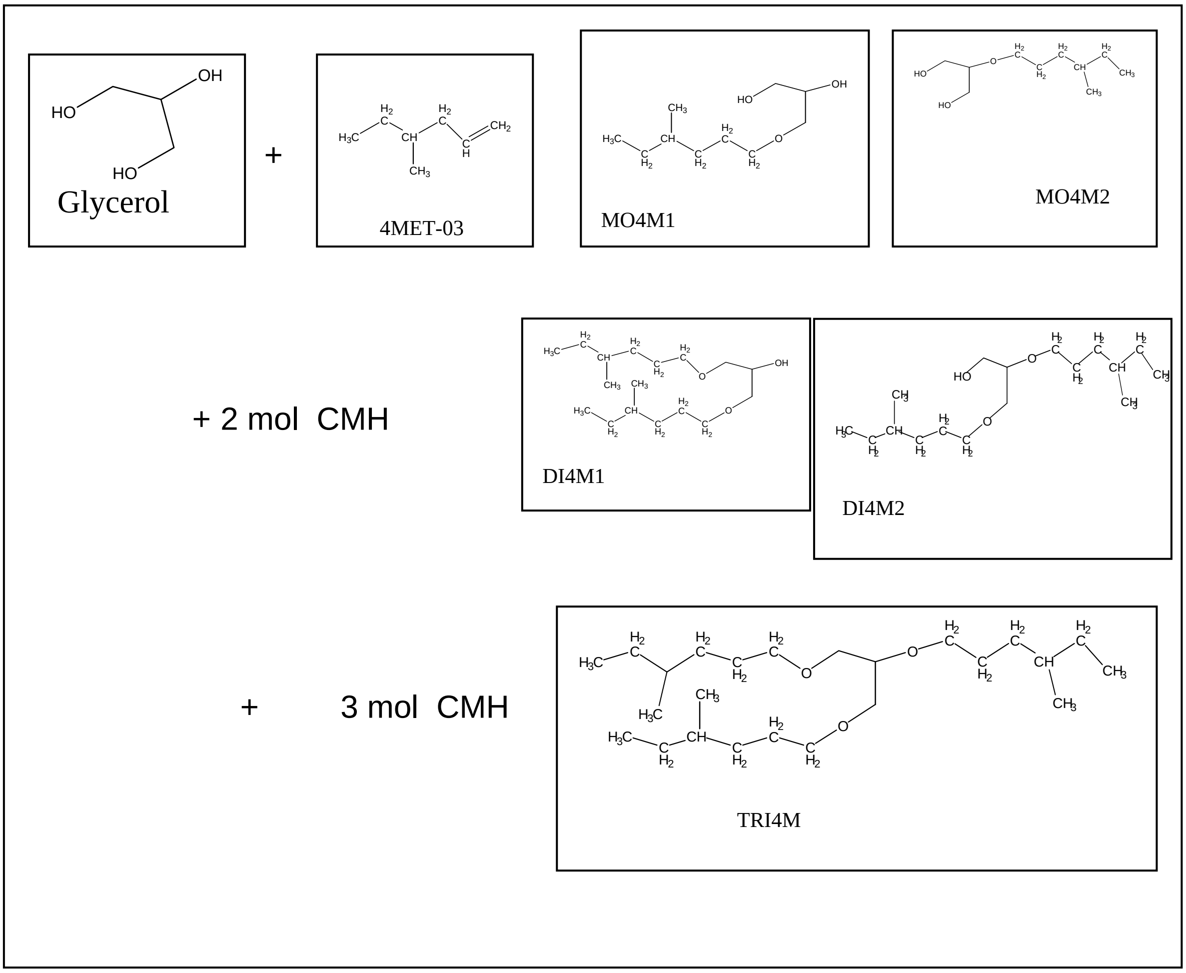


Figure5.16 Reaction products of glycerol with 4-methyl-1-hexene

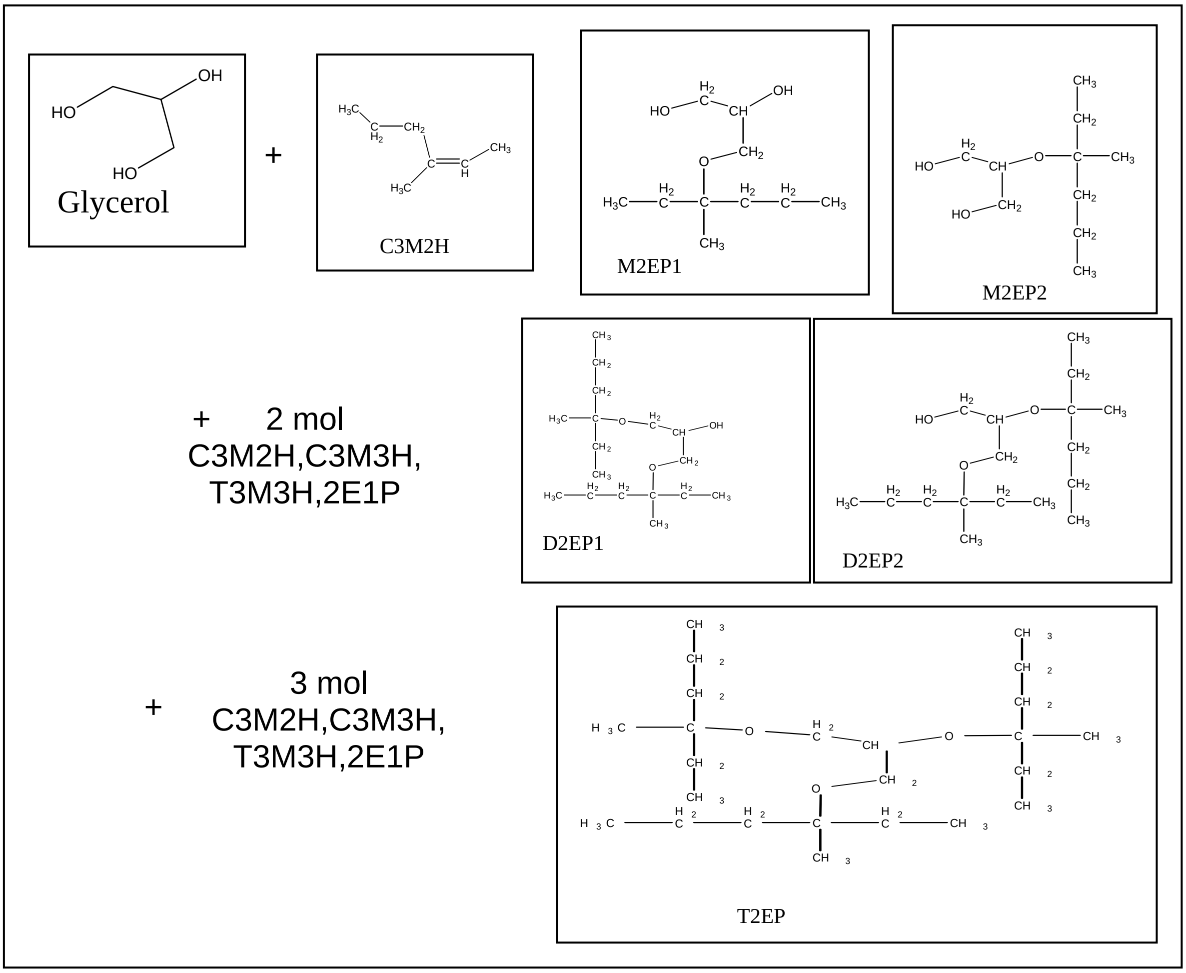


Figure5.17 Reaction products of glycerol with cis-3-methyl-2-hexene, cis-3-methyl-3-hexene, trans-3-methyl-3-hexene and 2-ethyl-1-pentene

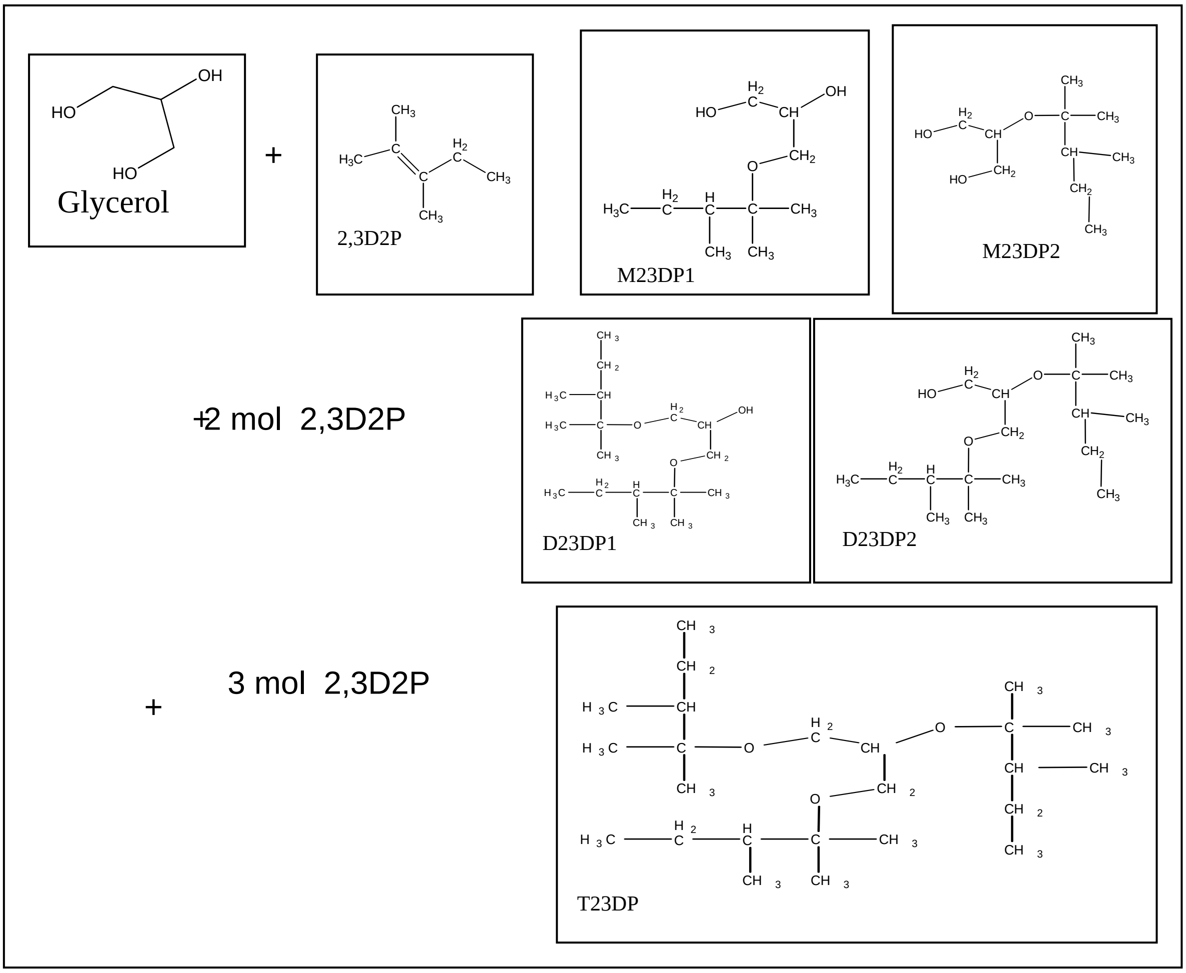


Figure5.18 Reaction products of glycerol with 2,3-dimethyl-2-pentene

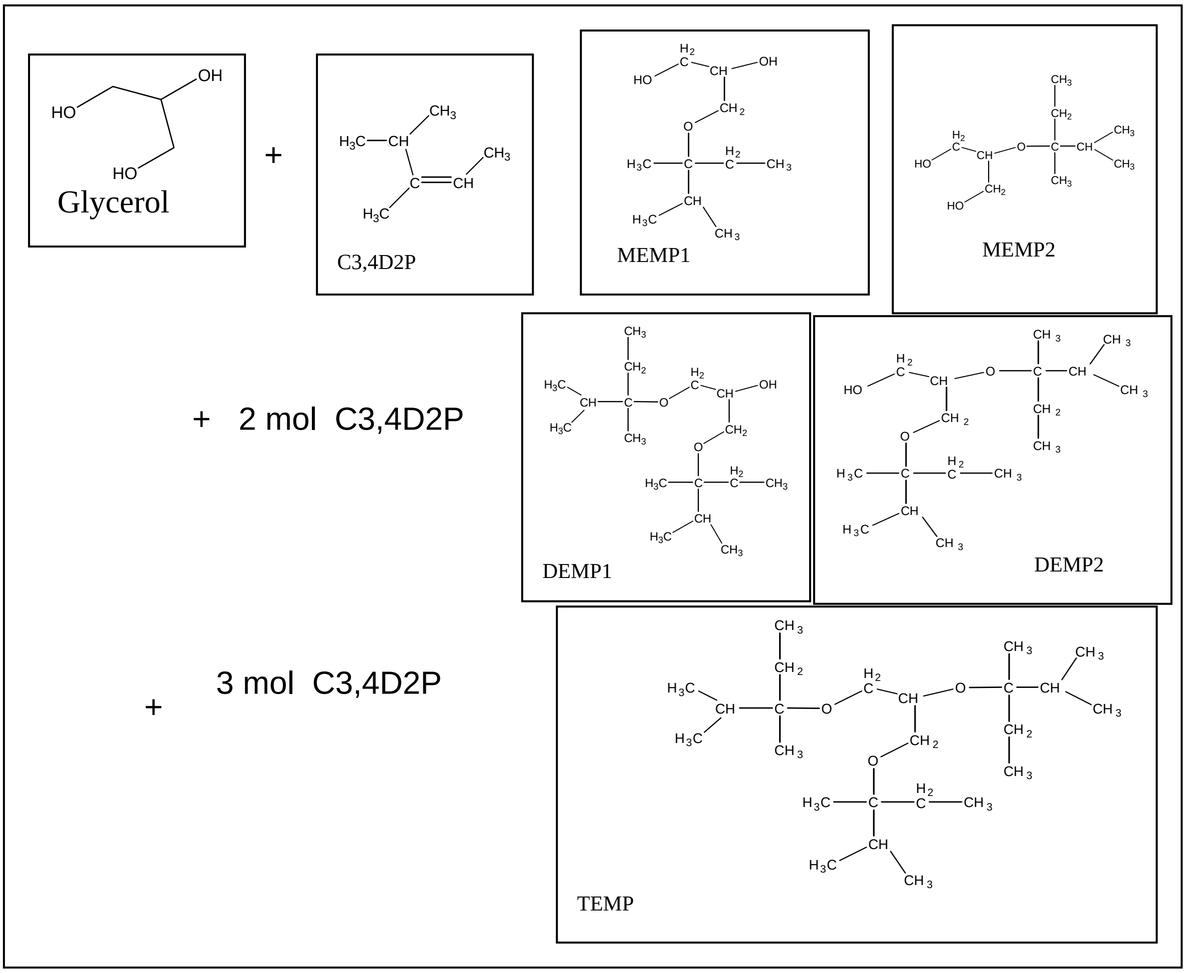


Figure5.19 Reaction products of glycerol with cis-3,4-dimethyl-2-pentene and 2-ethyl-3-methyl-1-butene

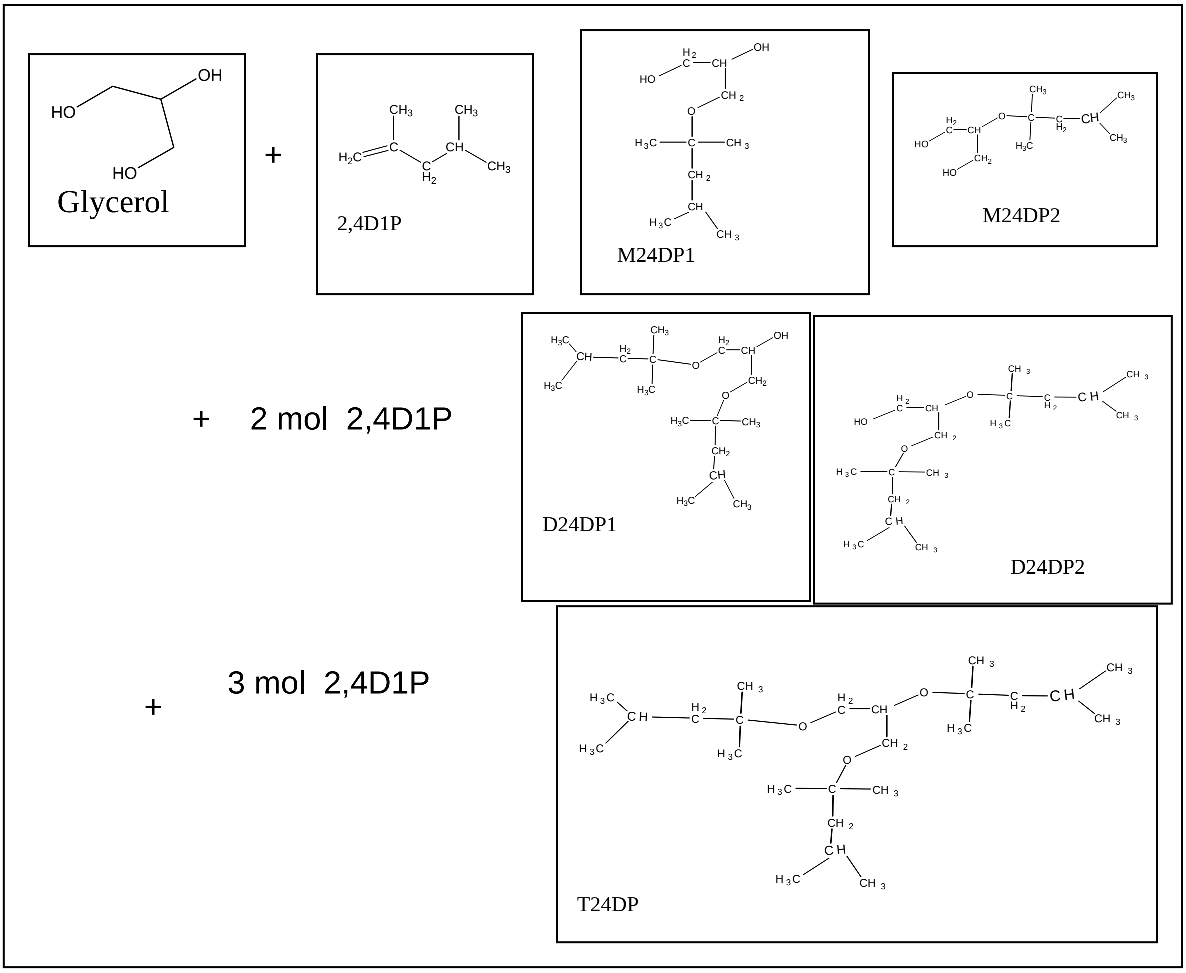


Figure5.20 Reaction products of glycerol with 2,4-dimethyl-1-pentene

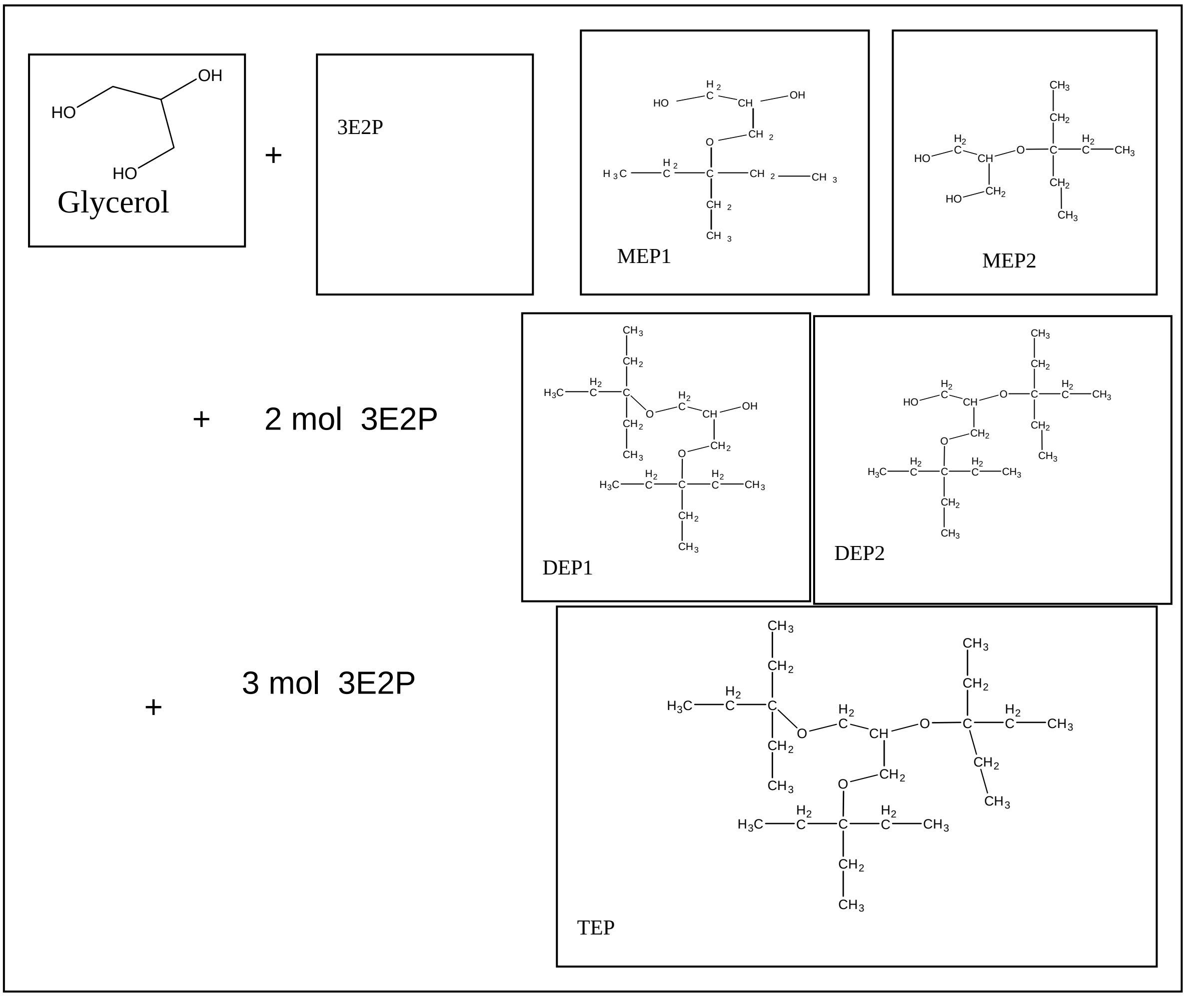
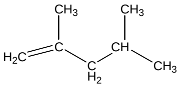


Figure5.21 Reaction products of glycerol with 3-ethyl-2-pentene

5.3.1 Normal boiling point

To predict the normal boiling point, many group contribution methods were applied. However, most of group contribution methods have a serious problem that they cannot distinguish among structural isomers because the isomers are in the same subgroup. As a result, the calculated properties are inevitably the same. The type of group contribution method can be divided in zero order, first order and second order. The basic level uses first order contributions while the higher level uses a small set of second order groups having the first order groups as building blocks. Dalmazzone et al. (2006) found that the second order group contribution method can predict the more accurate result than the first-order group contribution method. In this research, two group contribution methods (i.e. Joback's and Gani's method) were used for calculation of normal boiling point. It should be noted that Joback’s method is the first order group contribution method while Gani’s method is a combination of first order and second order group contribution method.

Table 5.4 The subgroup from Joback’s and Gani’s group contribution method of 2,4-dimethyl-1-pentene

Component	Group method	Subgroup				
		First order				Second order
	Joback’s	CH_3(1) , CH_2(2) , CH (3) CH_2=(1) , C=(3)				-
	Gani’s	CH_3(1)	CH_2(2)	CH_2=C(2)	CH (3)	(CH_3)2CH

An example of 2,4-dimethyl-1-pentene in C7 olefin is investigated. The numbers of subgroups and its value from different group methods are shown in Table 5.4 and 5.5, respectively. The obtained normal boiling points are 356.26 K, 355.68 K and 365.1 K from Gani’s method, Joback’s method and Pescarollo et al., respectively**.**

Table 5.5 The values of subgroup group from Joback’s and Gani’s group contribution method of 2,4-dimethyl-1-pentene for calculating normal boiling point

Subgroup type	Joback’s	Gani’s
	Tb	Tb
CH_3 (1)	23.58	-
CH_2 (2)	22.88	-
CH (3)	21.74	
CH2=(1)	18.18	-
C=(3)	24.14	-
CH3(1)	-	0.8894
CH2(2)	-	0.9225
CH (3)		0.6033
CH2=C(2)	-	1.7117
$(CH_3)_2CH$	-	-0.1157

The values of normal boiling point of reactive olefins taken from Pescarollo et al. (1993) were compared with the calculated normal boiling point from Gani’s method and Joback’s method as presented in Figure 5.22. The result shown that the predicted normal boiling points from both Joback’s method are in good agreement with the values from literatures, however from Gani's method aren't same the values from literatures while that of Gani's method give mostly higher value.

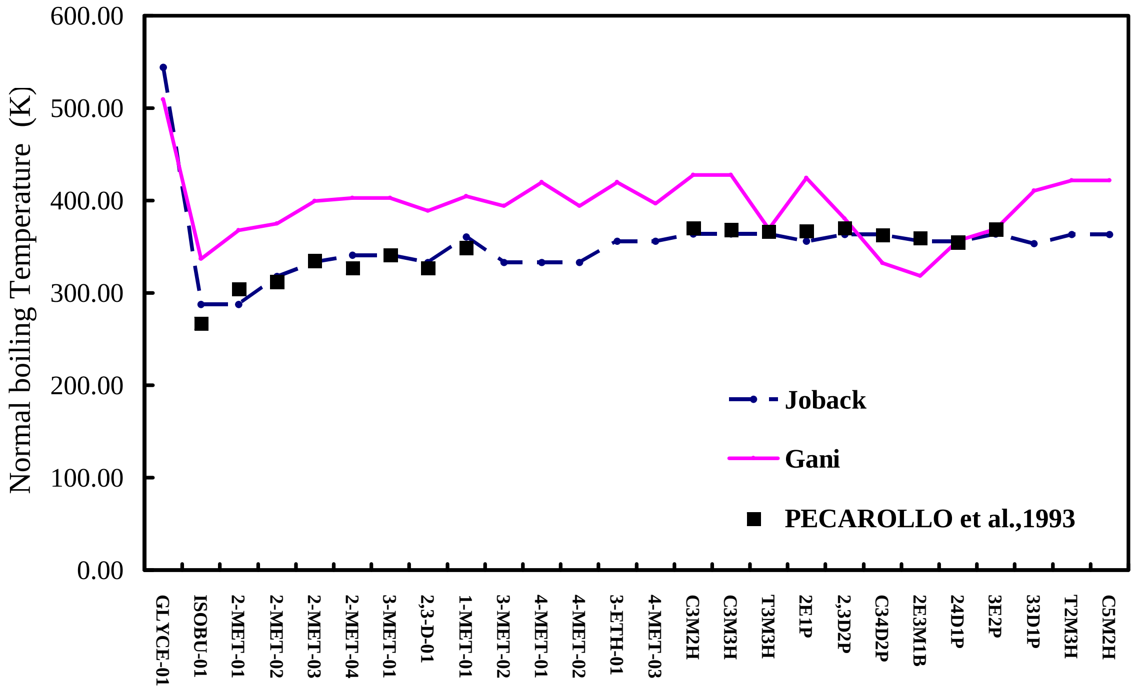


Figure 5.22 Normal boiling temperatures of reactive olefins

Figure 5.23 shows predicted normal boiling points of the etherified products from both Joback's method and Gani's method. However, it should be noted that no available data of oxygenates is currently present for comparing with the predicted value. The values of normal boiling point from Joback's method and Gani's method has the same trend of ethers for each atomic number of iso-olefins as monoethers < diethers < triether. However, Gani's method could not estimate the normal boiling point in some ether product. Therefore, conclusively, Joback's method is more preferable for estimating normal boiling point of reactive olefins and oxygenated ethers.

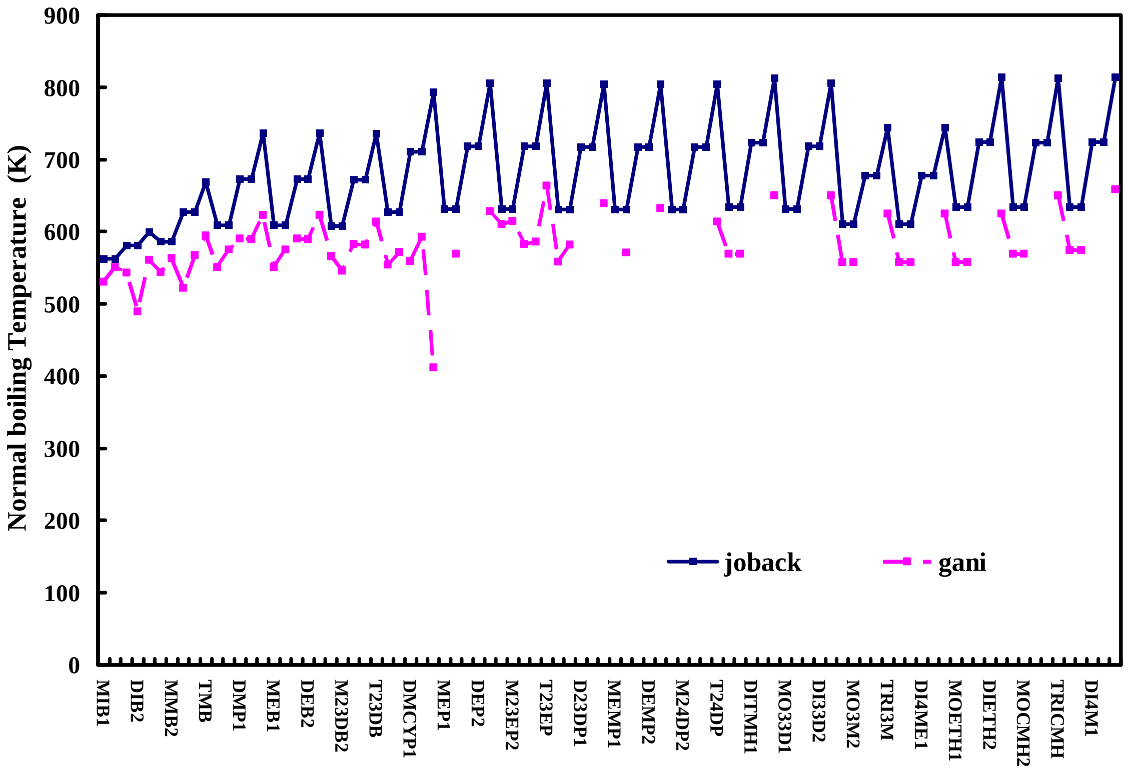


Figure 5.23 Normal boiling temperatures of etherified products

5.3.2 Critical properties

For calculation of critical temperature, the group contribution methods applied to estimate are Joback's method and Gani's method. Gani's method is more complex than Joback's method as described earlier. The results were compared with properties from the Handbook.

The example of counting subgroup for critical temperature with different group contribution methods was shown in Table 5.6. The critical temperatures of 2,4-dimethyl-1-pentene obtained from Joback's method, Gani's method and literature are 530.11 K, 523.80 K and 538 K, respectively.

Table 5.6 The values of subgroup from Joback's and Gani's group contribution method of 2,4-dimethyl-1-pentene for calculating critical properties

Subgroup type	Joback's		Gani's	
	Tc(K)	Pc(bar)	Tc(K)	Pc(bar)
First order group				
Alkyl carbon	-	-	-	-
>C<	-	-	-	-
Double bond	-	-	-	-
CH3(1)	0.0282	-0.0012	-	-
CH2(2)	0.0567	0	-	-
CH (3)	0.0164	0.0020	-	-
CH2=(1)	0.0113	-0.0028	-	-
C=(3)	0.0117	0.0011	-	-
CH3(1)	-	-	1.6781	0.0199
CH2(2)	-	-	3.4920	0.0106
CH (3)	-	-	4.0330	0.0013
CH2=C(2)	-	-	6.5081	0.0223
Second order group				
$(CH_3)_2CH$	-	-	-0.5334	-0.000488

Figure.5.24 and 5.25 showed that critical temperature of reactive olefins and etherified products, respectively. The different trend of two methods can be observed in both reactive olefins and etherified products. Critical temperature predicted by Joback's method showed similar values to that obtained Chemical Engineering Research Information Center (CHERIC). As shown in Fig 5.25, predicted critical temperature from Joback's method gave higher value than that of Gani's method , however, similar trend for each atomic number of iso-olefins as monoethers < diethers < triether were observed. However, again, Gani's method could not estimate critical temperature in some ether product.

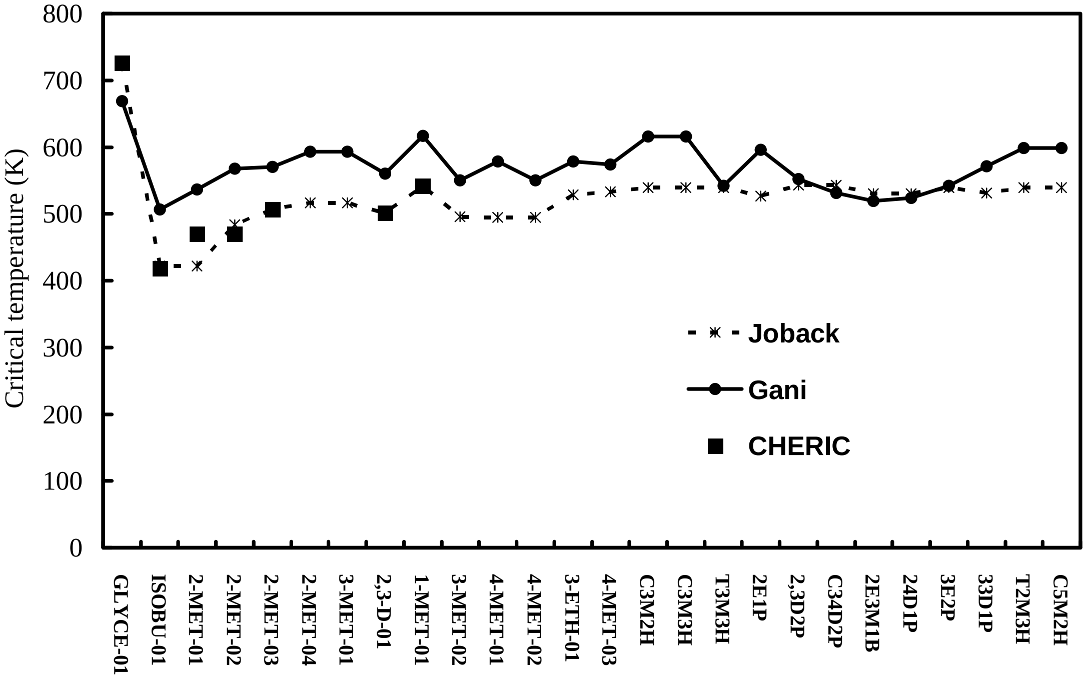


Figure 5.24 Critical temperatures of reactive olefins

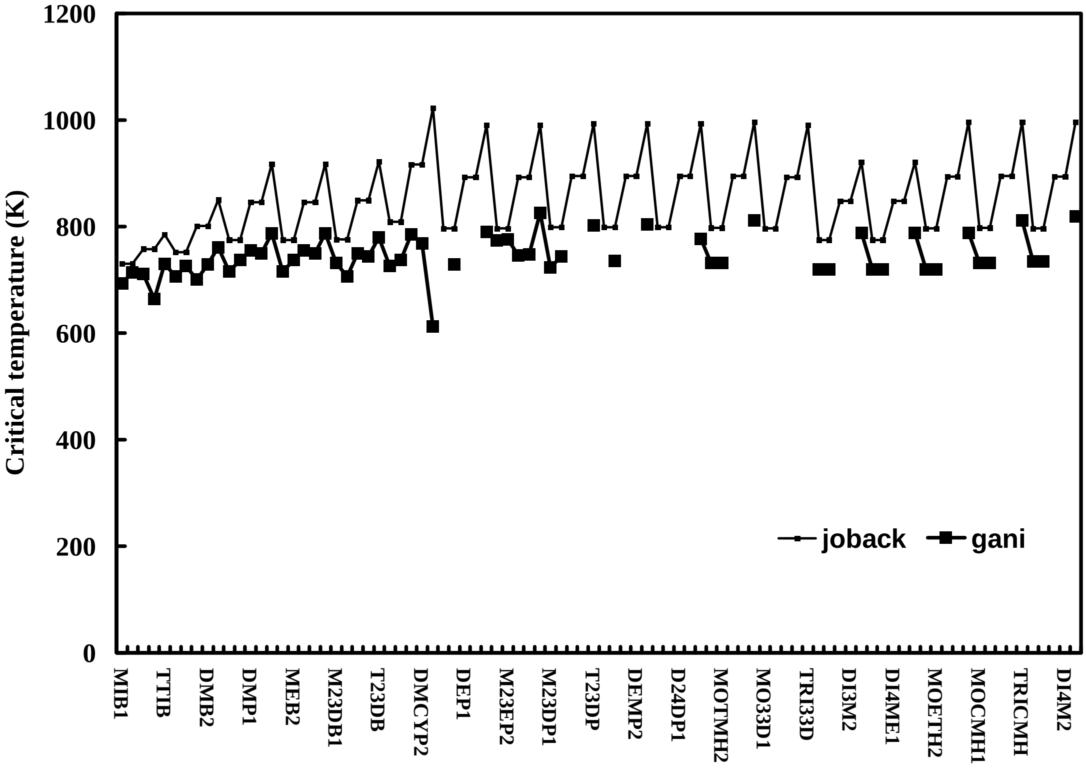


Figure 5.25 Critical temperatures of etherified products

Figure 5.26 and Figure 5.27 showed critical pressures of reactive olefins and etherified products, respectively. As shown in Fig. 5.26, again, Joback's method gave a value closer to the CHERIC Handbook than that of Gani's method.

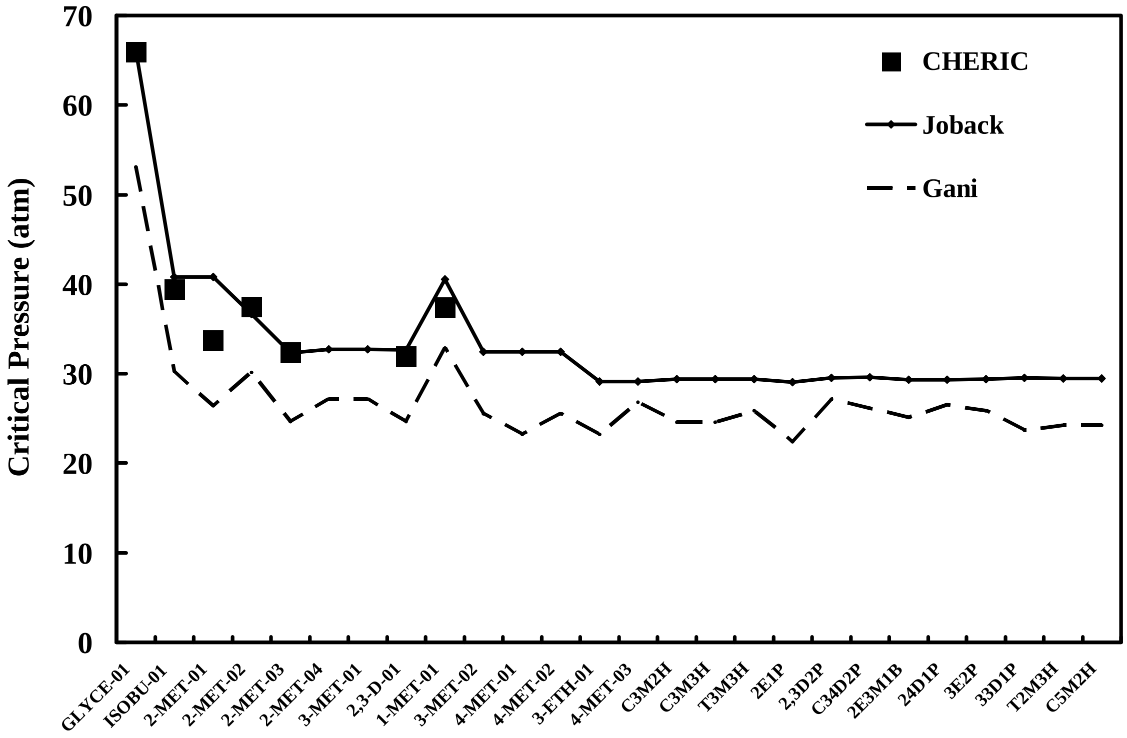


Figure 5.26 Critical pressures of reactive olefins

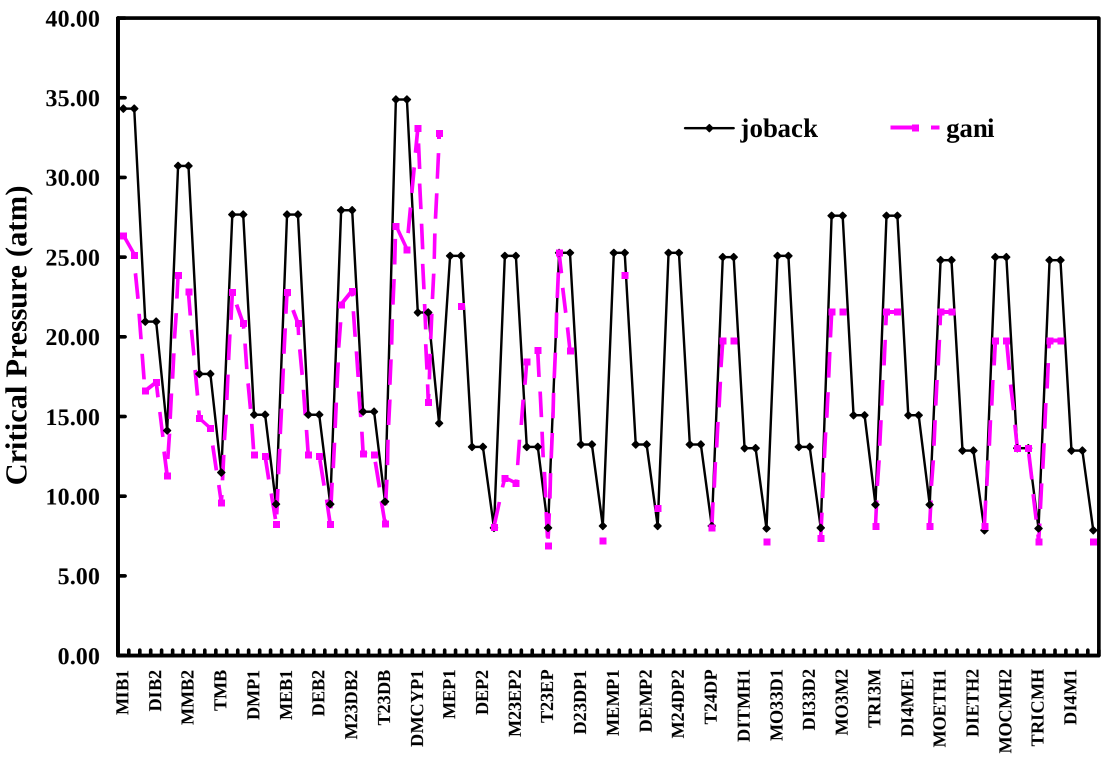


Figure 5.27 Critical pressures of etherified products

5.3.3 Gibbs of formation

For calculation of Standard Gibbs free energy of formation, Joback's method, Gani's method and Benson's method were investigated. Standard Gibbs free energy of formation is the most important property for RGibbs reactor which minimizes Gibbs free energy of formation of each component in the studied system. Higher order group contribution methods are expected to give more precise predictions; therefore, the Benson's method is the most precise group contribution method for thermo chemical data computation. Nevertheless, a much greater number of contributions are needed. To predict the properties of isomer molecules, the methods are exclusively based on the molecular structure of the compounds in order that the methods are able to distinguish among isomers. Therefore, the method for predicting Gibbs free energy of formation needs the higher order. The results of Gibbs free energy of formation using first order (Joback's method), first-second order (Gani's method), and second order (Benson's method) are illustrated in Figure 5.28 and Figure 5.29. As shown in Fig. 5.28, only Joback's and Benson's method gave a predicted of Gibbs free energy of formation closed to the literature.

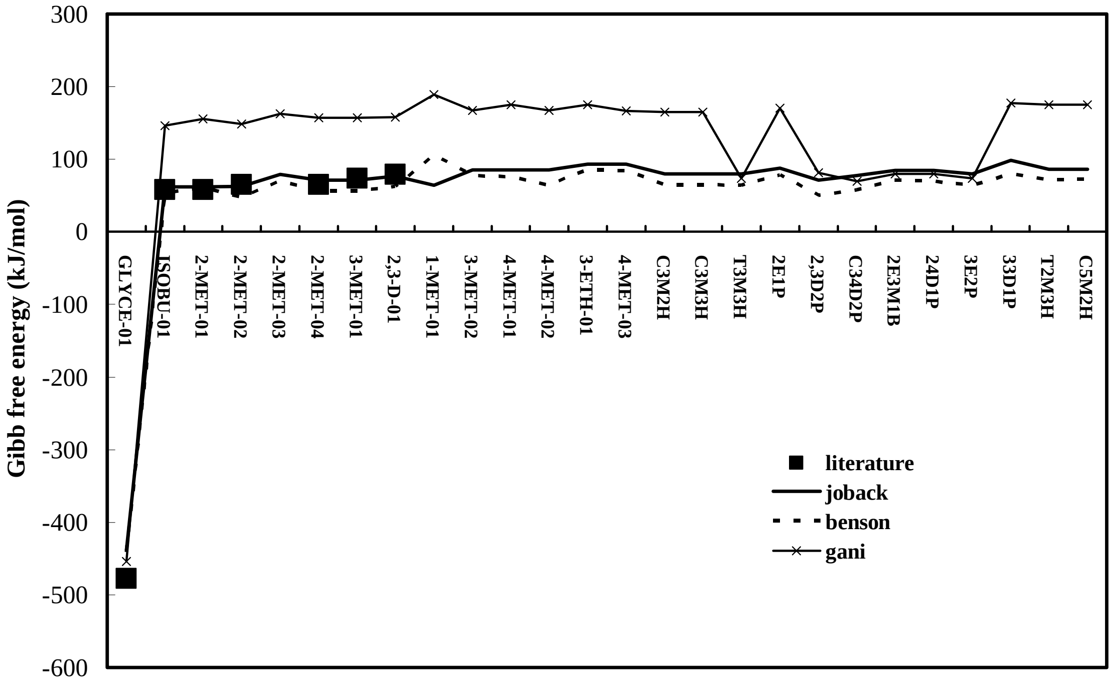


Figure 5.28 Gibbs free energy of formation of reactive olefins

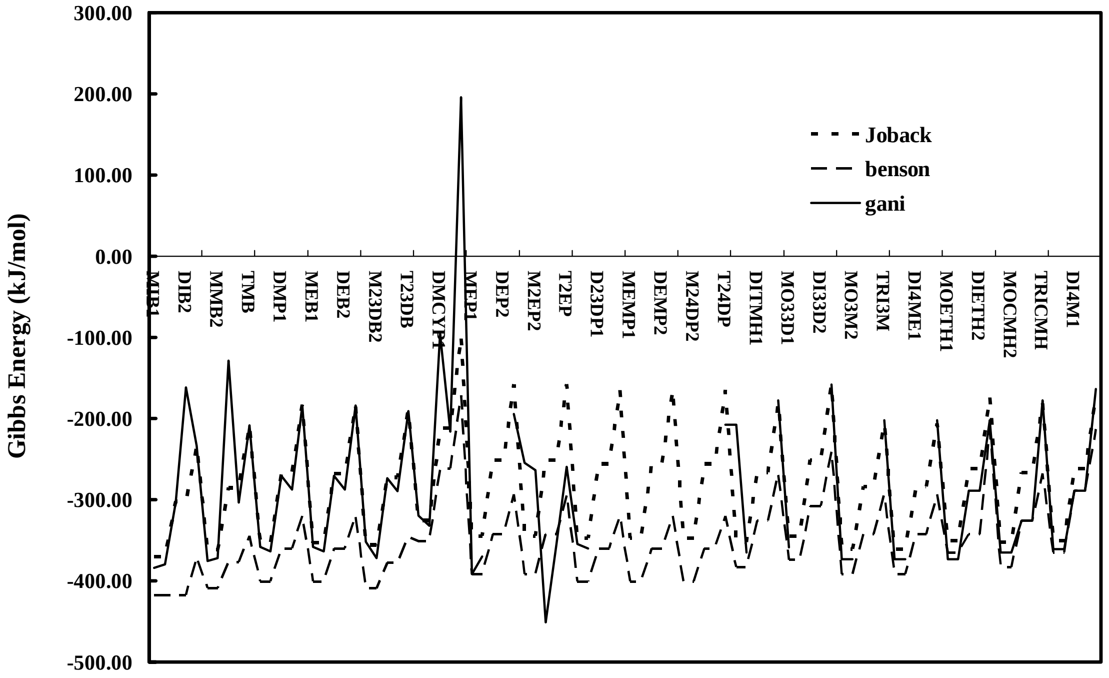


Figure 5.29 Gibbs free energy of formation of etherified products

5.4 Comparison of equilibrium conversion between experimental and thermodynamic modeling.

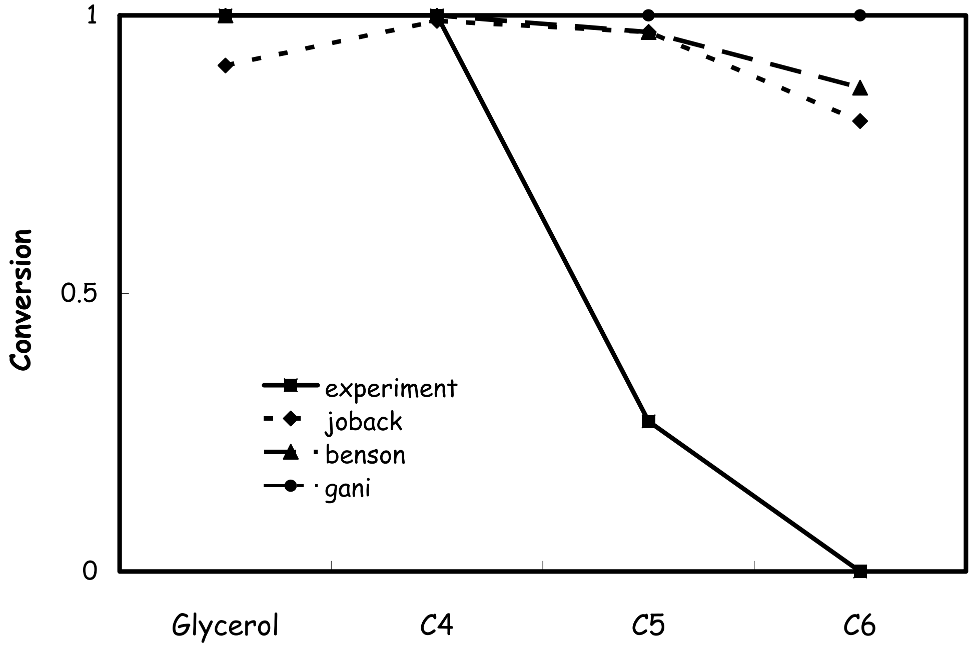


Figure 5.30 Comparison of equilibrium conversion between experimental and thermodynamic modeling.

Figure 5.32 showed a comparison of equilibrium conversion between experimental and thermodynamic modeling. As shown in Fig 5.30, under the assumption of etherification between glycerol and iso-olefins and isomerization among olefinic compounds which are the scope of the consideration in this study, all three group contribution method Joback, Gani and Benson predicted only the conversion of glycerol and C4 precisely. The predicted of C5-C6 conversion are quite far from the experimental results. However, comparing among the group contribution method, Joback's method give a more obvious view that with conversion of iso-olefins decreased with larger atomic number of iso-olefins.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusion

6.1.1 Experimental of etherification of FCC gasoline with glycerol

The etherification of FCC gasoline with glycerol showed a promising process for gasoline quality improvement and utilization of glycerol as a fuel extender simultaneously. The properties of FCC and etherified FCC products were determined by the standard analysis of Research Octane Number (RON), blending Reid vapor pressure (bRvp), distillation temperature following the standard methods of ASTM D -2699, ASTM D 5191-99 and ASTM D 86-05, respectively. The etherified FCC gasoline showed higher research octane number (RON) and lower blending Reid vapor pressure (bRvp) which are preference properties. The suitable operating condition of reaction were carried out by feeding FCC to glycerol ratio of 4:1 with operating temperature of 70°C, 10 g of Amberlyst 16 catalyst and 10 hours of reaction time.

6.1.2 Thermodynamic modeling of etherification of FCC gasoline with glycerol

The thermodynamic modeling study of etherification reactions between gasoline from fluidized catalytic cracking and glycerol was investigated by using a simulation program, Aspen plus version 11.1. The group contribution methods (i.e. Joback’s method, Gani’s method and Benson’s method) were applied to estimate the missing parameters (e.g. critical pressure, critical temperature, boiling point, stardard Gibb’s free energy of formation). The preliminary selection of group contribution method shows that Joback’s method are well-predicted for normal boiling point, critical temperature, and critical pressure and standard Gibb’s free energy of formation. However, using the group contribution method to estimate conversion give good agreement for only glycerol and C4 olefin while C5-C6 olefins conversion are quite far from the experimental results.

6.2 Recommendations

Due to the limitation of glycerol can be added to fuel oil. However, RON of etherified FCC gasoline is quite low for use in fuel. Therefore, the RON improvement might be only due to the etherification with glycerol. On the contrary, the bRvp of etherified FCC with glycerol are lower than that of etherified with 20 % vol ethanol. The reduction of bRvp is beneficial especially for hot countries or in summer. Thus, the etherification of FCC gasoline with glycerol for gasoline quality improvement and utilization of glycerol as a fuel extender simultaneously that the suitable for hot countries.

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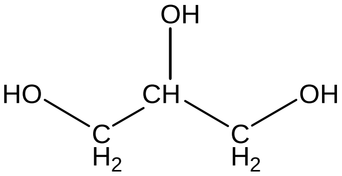
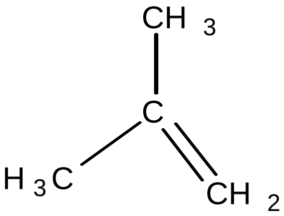
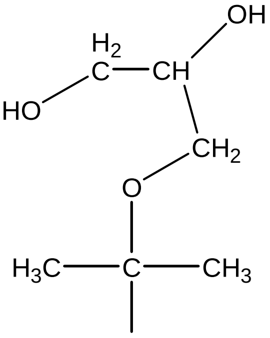
APPENDIX

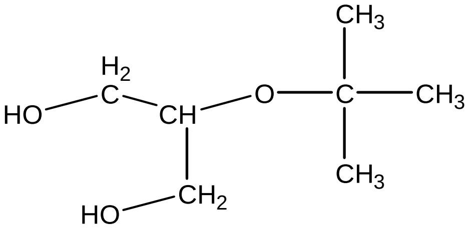
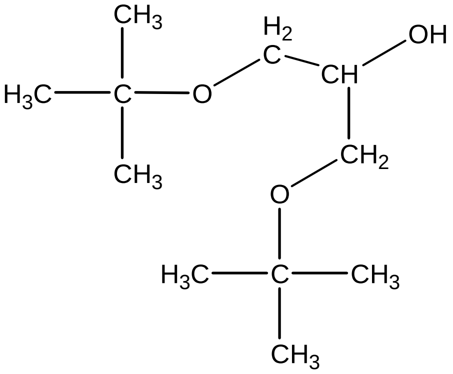
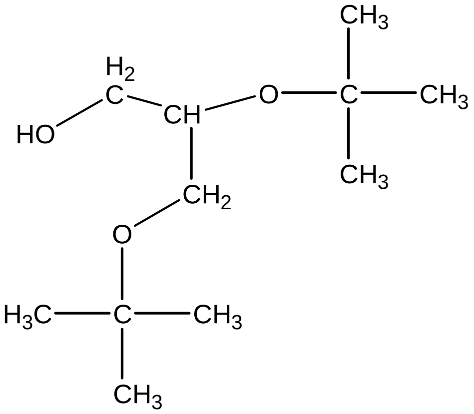
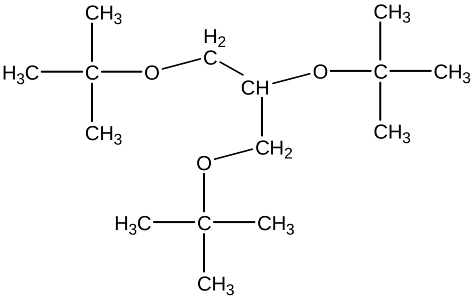
APPENDIX A

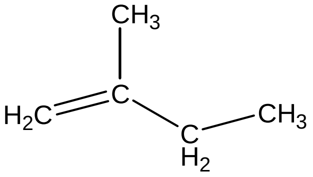
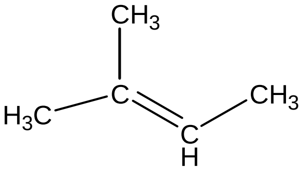
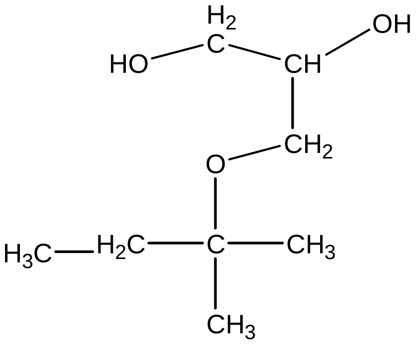
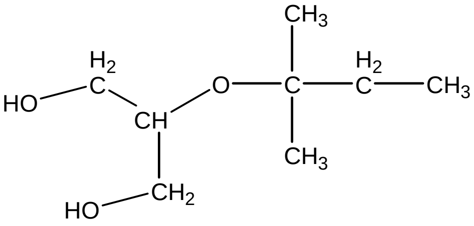
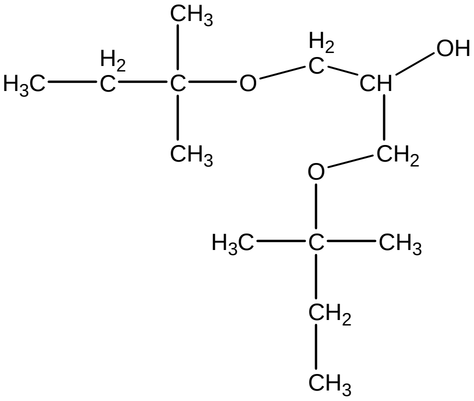
JOBACK'S GROUP CONTRIBUTION METHOD

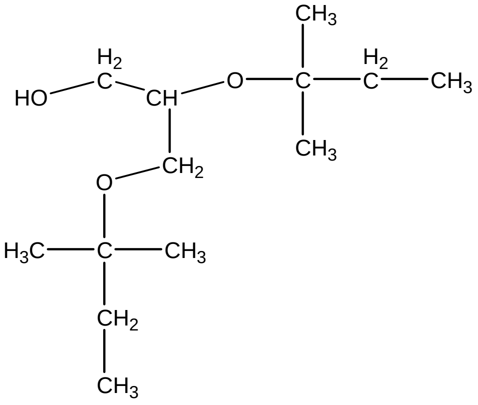
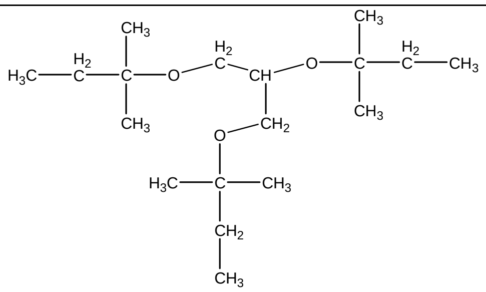
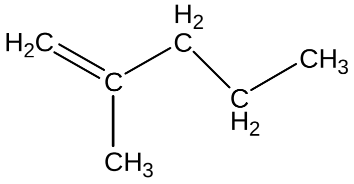
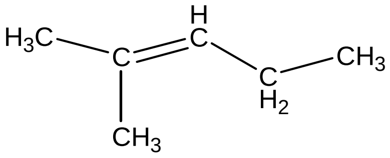
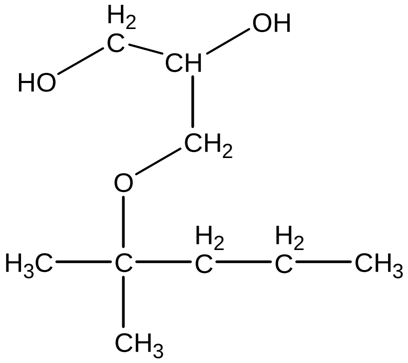
The functional groups of components in olefins are listed below with the number of subgroup in each component. Joback's group contribution method will be used to estimate the property of olefin components. This method can be used to estimate critical properties such as critical temperature and critical pressure or normal boiling point or estimated the thermodynamic properties such as Gibbs of formation.

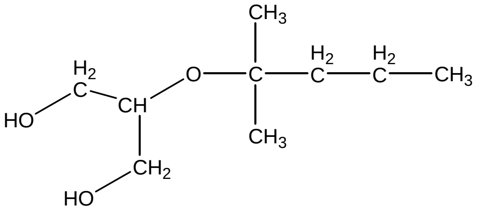
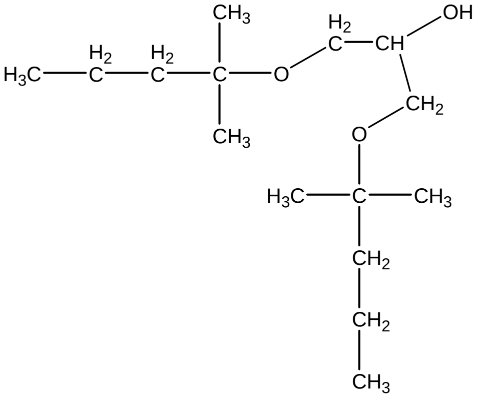
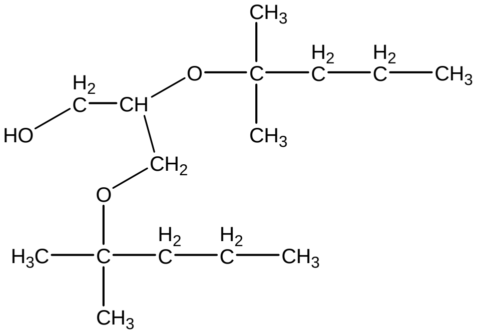
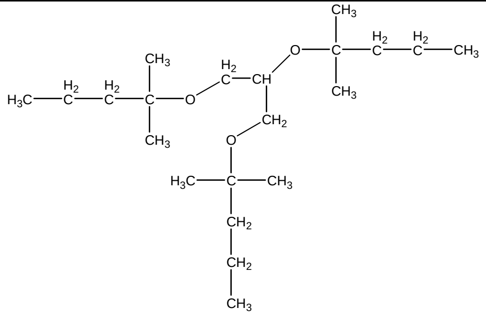
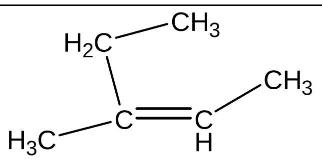
Table C. Sub group of components

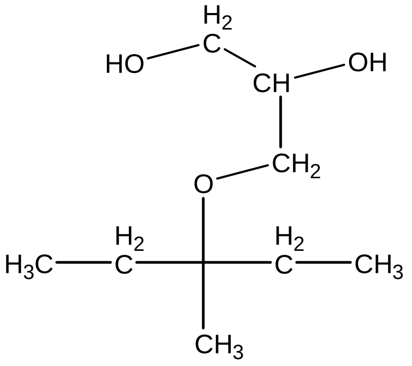
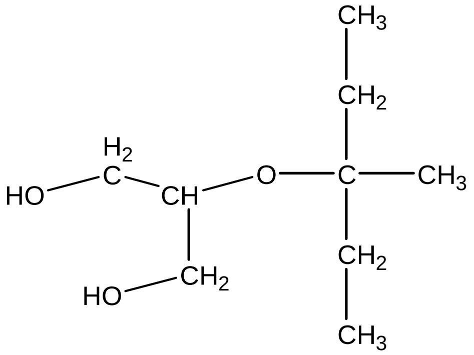
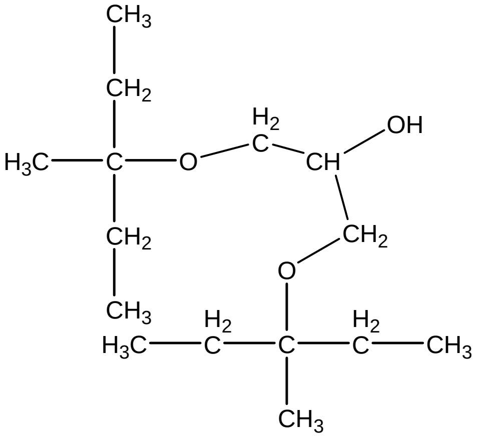
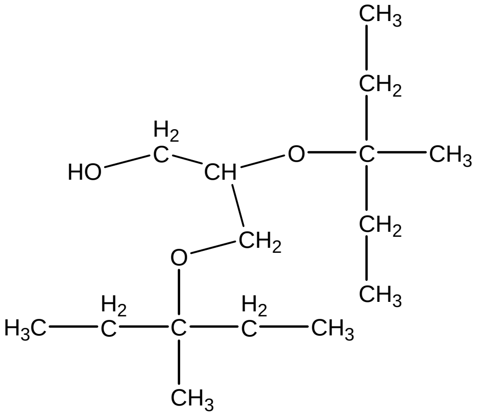
Name	Structure	Sub group
Glycerol		$>CH_2$:2 $>CH$: 1 $-OH$: 3
Isobutene		CH_3: 2 $=CH_2$: 1 $=C<$: 1
3-tert-butoxy -1,2-propanediol		CH_3: 3 CH_2:2 CH: 1 $>C<$: 1 O: 1 $-OH$:2

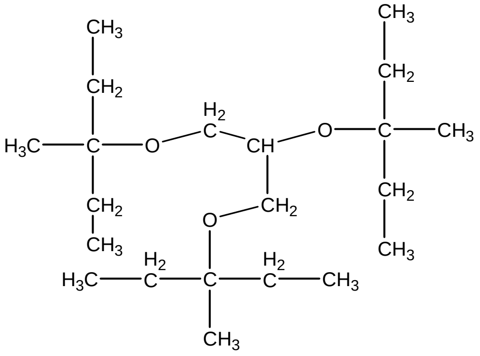
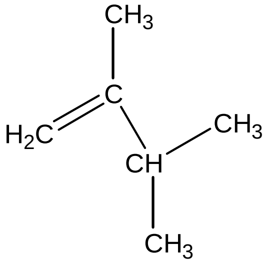
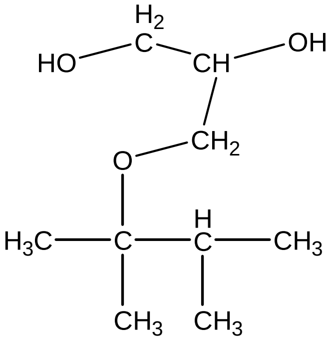
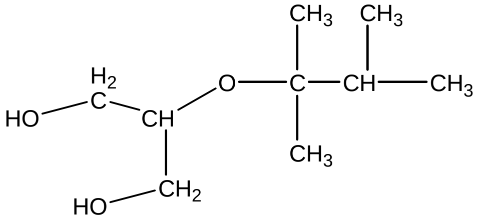
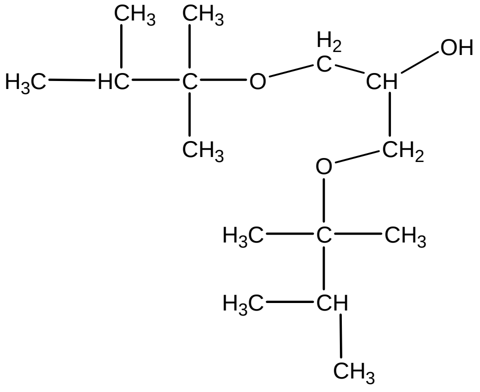
Name	Structure	Sub group
2-tert-butoxy -1,3-propanediol		CH_3: 3 CH_2:2 CH: 1 >C<: 1 O: 1 -OH :2
1,3-di-tert-butoxy-2-propanol		CH_3: 6 CH_2:2 CH: 1 >C<: 2 O: 2 -OH :1
2,3-di-tert-butoxy-1-propanol		CH_3: 6 CH_2:2 CH: 1 >C<: 2 O: 2 -OH :1
1,2,3- tri-tert-butoxy-propane		CH_3: 9 CH_2:2 CH: 1 >C<: 3 O: 3

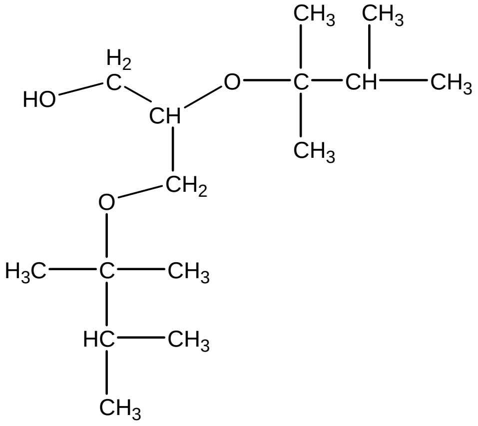
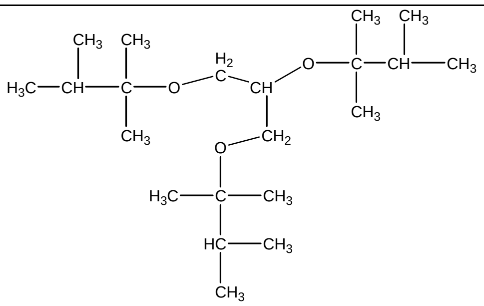
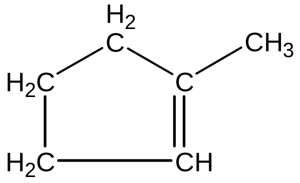
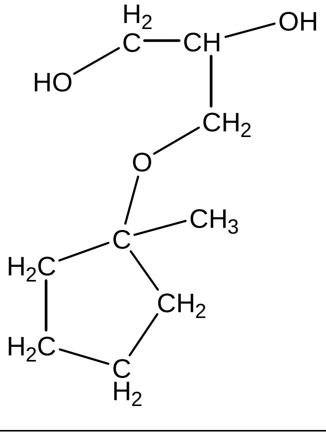
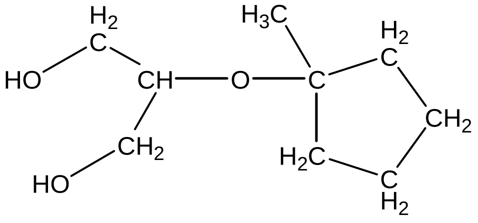
Name	Structure	Sub group
2-methyl-1-butene		CH3 : 2 >CH2: 1 =CH2 :1 =C< : 1
2-methyl-2-butene		CH3 : 3 =CH :1 =C< : 1
3(1,1-dimethyl-propoxy)-1,2-propanediol		CH_3: 3 CH_2:3 CH: 1 >C<: 1 O: 1 -OH :2
2(1,1-dimethyl-propoxy)-1,3-propanediol		CH_3: 3 CH_2:3 CH: 1 >C<: 1 O: 1 -OH :2
1,3-bis-(1,1-dimethyl propoxy) -2-propanol		CH_3: 6 CH_2:4 CH: 1 >C<: 2 O: 2 -OH :1

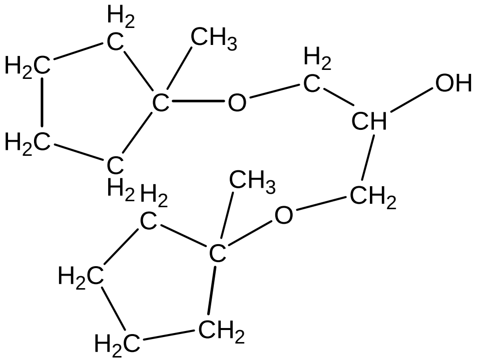
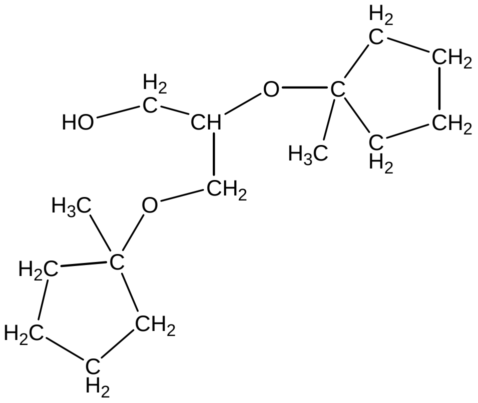
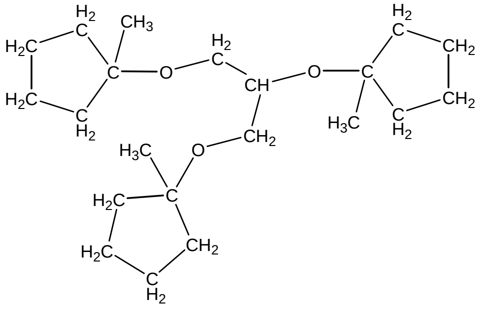
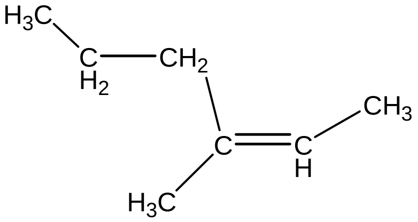
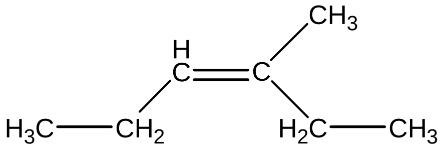
Name	Structure	Sub group
2,3-bis-(1,1-dimethyl propoxy) -1-propanol		CH_3: 6 CH_2:4 CH: 1 >C<: 2 O: 2 -OH :1
1,2,3-tris-(1,1-dimethyl propoxy)-propane		CH_3: 9 CH_2:5 CH: 1 >C<: 3 O: 3
2-methyl-1-pentene		CH3 : 2 >CH2: 2 =CH2 :1 =C< : 1
2-methyl-2-pentene		CH3 : 3 >CH2: 1 =CH :1 =C< : 1
3-(1,1-dimethyl butoxy)-1,2-propanediol		CH_3: 3 CH_2:4 CH: 1 >C<: 1 O: 1 -OH :2

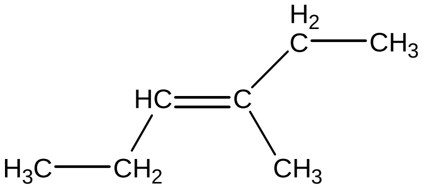
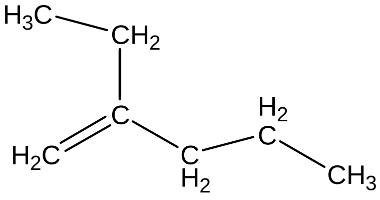
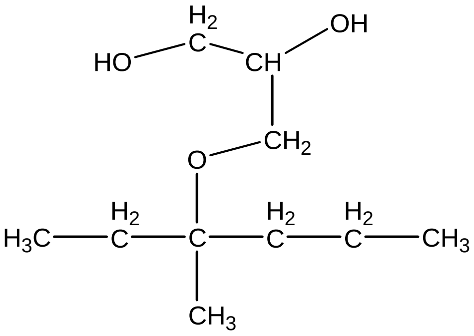
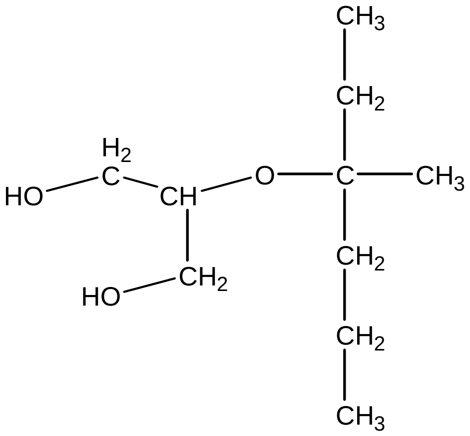
Name	Structure	Sub group
2-(1,1-dimethyl butoxy)-1,3-propanediol		CH_3: 3 CH_2:4 CH: 1 >C<: 1 O: 1 -OH :2
1,3-bis (1,1-dimethyl butoxy)-2-propanol		CH_3: 6 CH_2:6 CH: 1 >C<: 2 O: 2 -OH :1
2,3-bis (1,1-dimethyl butoxy)-1-propanol		CH_3: 6 CH_2:6 CH: 1 >C<: 2 O: 2 -OH :1
1,2,3-tris(1,1-dimethyl butoxy)-propane		CH_3: 9 CH_2:8 CH: 1 >C<: 3 O: 3
cis-3-methyl-2-pentene		CH3 : 3 >CH2: 1 =CH :1 =C< : 1

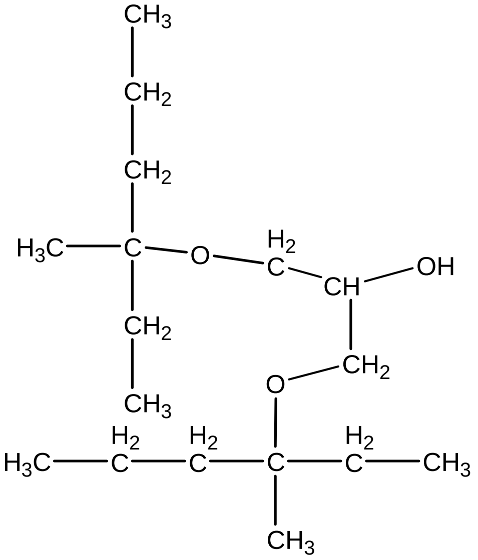
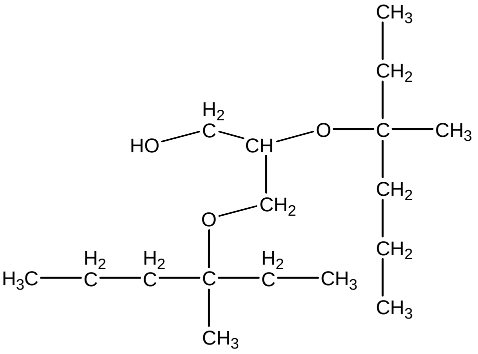
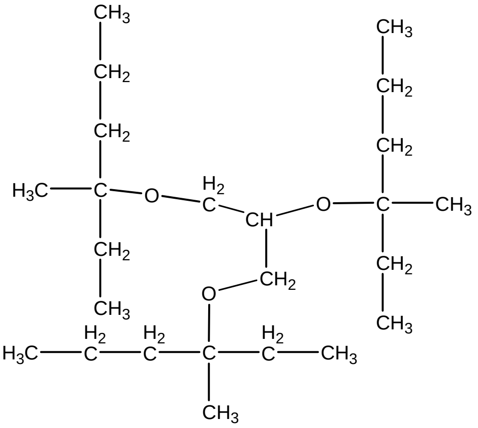
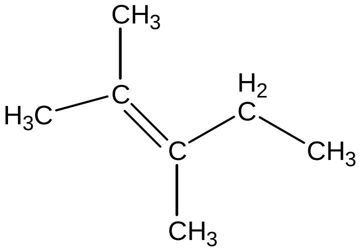
Name	Structure	Sub group
3-(1-methyl-2-ethyl-propoxy)-1,2-propanediol		CH_3: 3 CH_2:4 CH: 1 >C<: 1 O: 1 -OH :2
2-(1-methyl-2-ethyl-propoxy)-1,3-propanediol		CH_3: 3 CH_2:4 CH: 1 >C<: 1 O: 1 -OH :2
1,3-bis (1,1-methyl-2-ethyl-propoxy)-2- propanol		CH_3: 6 CH_2:6 CH: 1 >C<: 2 O: 2 -OH :1
2,3-bis (1,1-methyl-2-ethyl -propoxy)-1- propanol		CH_3: 6 CH_2:6 CH: 1 >C<: 2 O: 2 -OH :1

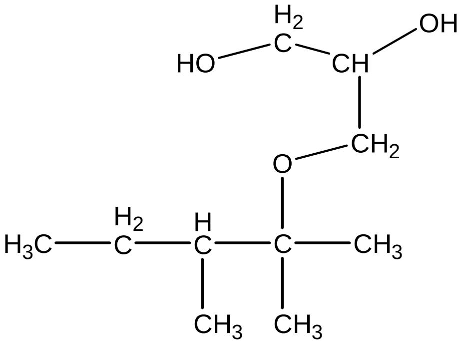
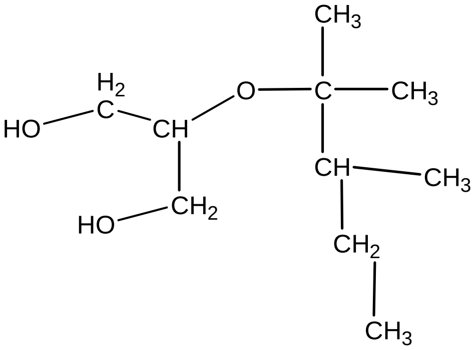
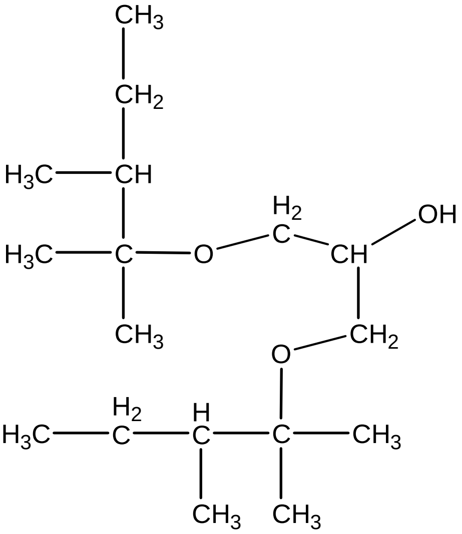
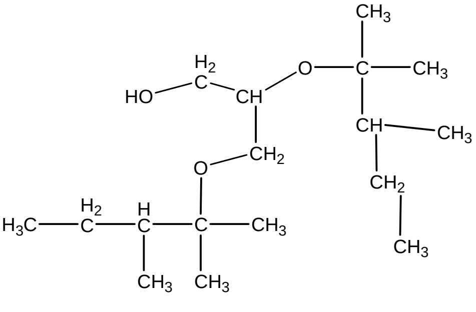
Name	Structure	Sub group
1,2,3-tris (1-methyl-2-ethyl-propoxy)- propane		CH_3: 9 CH_2:8 CH: 1 >C<: 3 O: 3
2,3-dimethyl-1-butene		CH3 : 3 >CH2: 1 =CH2 :1 =C< : 1
3-(1,1,2-trimethyl-propoxy)-1,2-propanediol		CH_3: 4 CH_2:2 CH: 2 >C<: 1 O: 1 -OH :2
2-(1,1,2-trimethyl-propoxy)-1,3-propanediol		CH_3: 4 CH_2:2 CH: 2 >C<: 1 O: 1 -OH :2
1,3-bis(1,1,2-trimethyl-propoxy)-2-propanol		CH_3: 8 CH_2:2 CH: 3 >C<: 2 O: 2 -OH :1

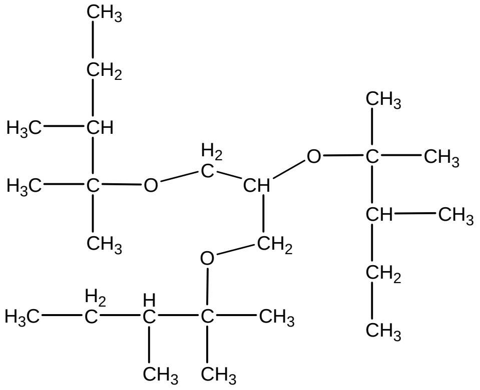
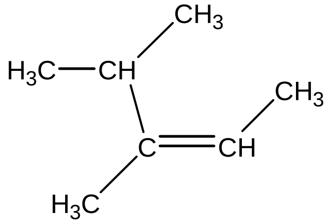
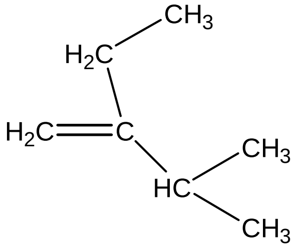
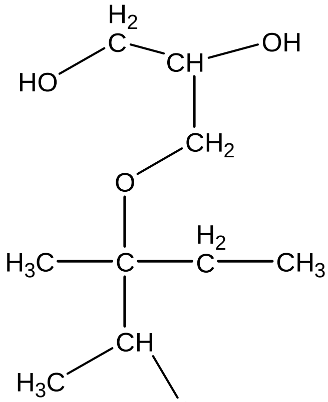
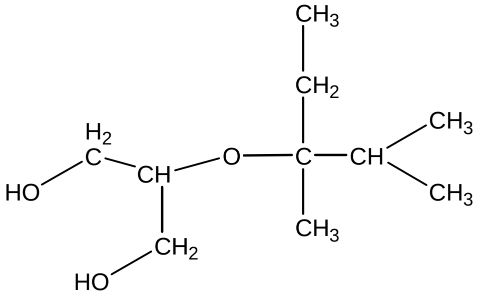
Name	Structure	Sub group
2,3-bis(1,1,2-trimethyl-propoxy)-1-propanol		CH_3: 8 CH_2:2 CH: 3 >C<: 2 O: 2 -OH :1
1,2,3-tris(1,1,2-trimethyl-propoxy)-propane		CH_3: 12 CH_2:2 CH: 4 >C<: 3 O: 3
1-methylcyclopentene		-CH3 :1 >CH2 :3 =CH- :1 =C<:1
3-(1,1,2-trimethyl-propoxy)-1,2-propanediol		CH_3: 1 CH_2:2 CH: 1 >CH2: 4 >C<:1 O: 1 -OH :2
2-(1,1,2-trimethyl-propoxy)-1,3-propanediol		CH_3: 1 CH_2:2 CH: 1 >CH2: 4 >C<:1 O: 1

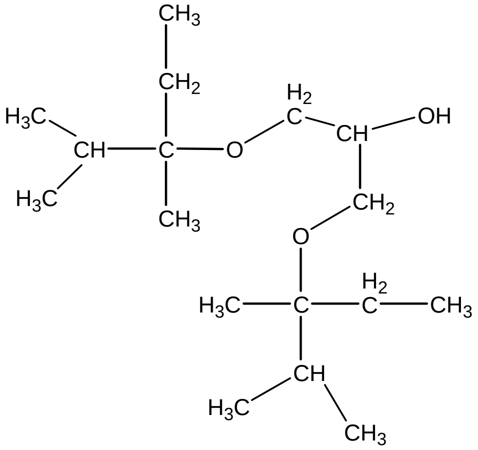
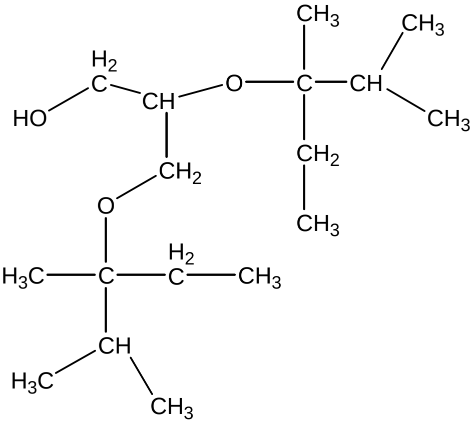
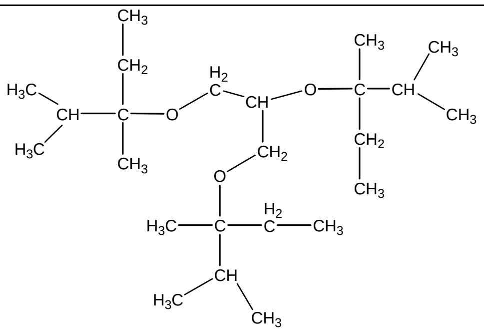
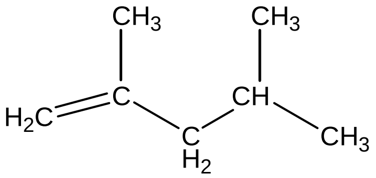
		-OH :2
Name	Structure	Sub group
1,3-bis-(1-methyl cyclopentyloxy)-2-propanol		CH_3: 2 CH_2:2 CH: 1 >CH2: 8 >C<:2 O: 2 -OH :1
2,3-bis-(1-methyl cyclopentyloxy)-1-propanol		CH_3: 2 CH_2:2 CH: 1 >CH2: 8 >C<:2 O: 2 -OH :1
1,2,3-tris(1-methyl cylopentyloxy)-propane		CH_3: 3 CH_2:2 CH: 1 >CH2: 12 >C<:3 O: 3
cis-3-methyl-2-hexene		CH3: 3 >CH2 :2 =CH : 1 =C< : 1
cis-3-methyl-3-hexene		CH3: 3 >CH2 :2 =CH : 1 =C< : 1

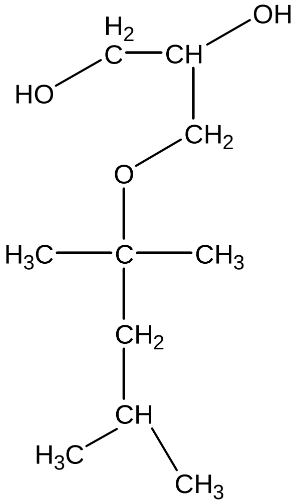
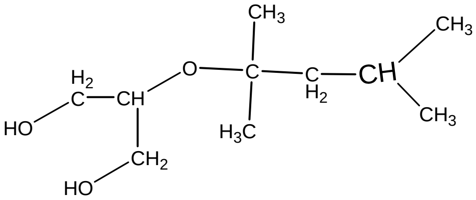
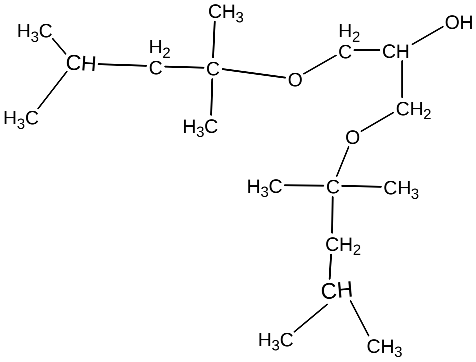
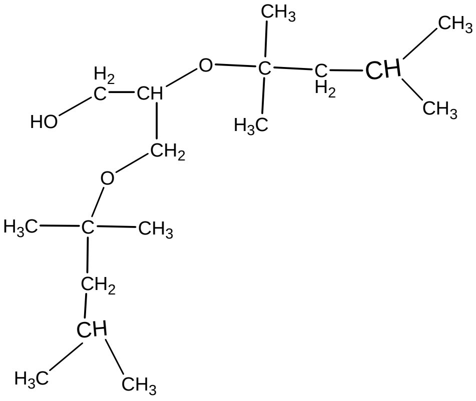
Name	Structure	Sub group
trans-3-methyl-3-hexene		CH3: 3 >CH2 :2 =CH : 1 =C< : 1
2-ethyl-1-pentene		CH3: 2 >CH2 :2 =CH2 : 1 =C< : 1
3-(1-methyl-1-ethyl-butoxy)-1,2-propanediol		CH$_3$: 3 CH$_2$:5 CH: 1 >C<: 1 O: 1 -OH :2
2-(1-methyl-1-ethyl-butoxy)-1,3-propanediol		CH$_3$: 3 CH$_2$:5 CH: 1 >C<: 1 O: 1 -OH :2

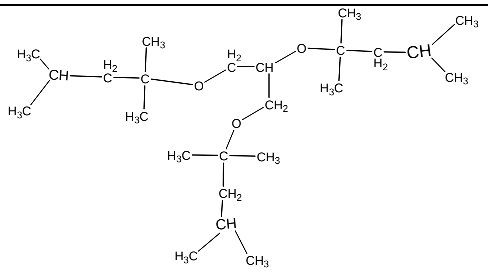
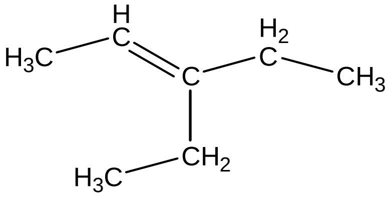
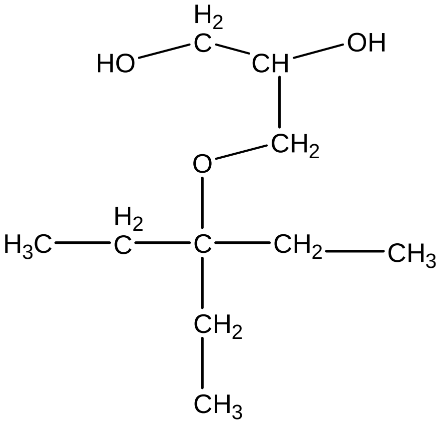
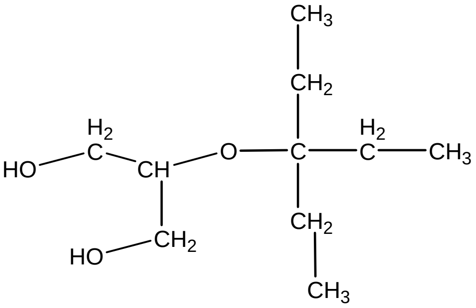
Name	Structure	Sub group
1,3-bis(1-methyl-1-ethyl-butoxy)-2-propanol		CH_3: 6 CH_2:8 CH: 1 >C<: 2 O: 2 -OH :1
2,3-bis(1-methyl-1-ethyl-butoxy)-1-propanol		CH_3: 6 CH_2:8 CH: 1 >C<: 2 O: 2 -OH :1
1,2,3-tris(1-methyl-1-ethyl-butoxy)- propane		CH_3: 9 CH_2:11 CH: 1 >C<: 3 O: 3
2, 3-dimethyl-2-pentene		CH3: 3 >CH2 :1 >CH- : 1 =CH2 : 1 =C< : 1

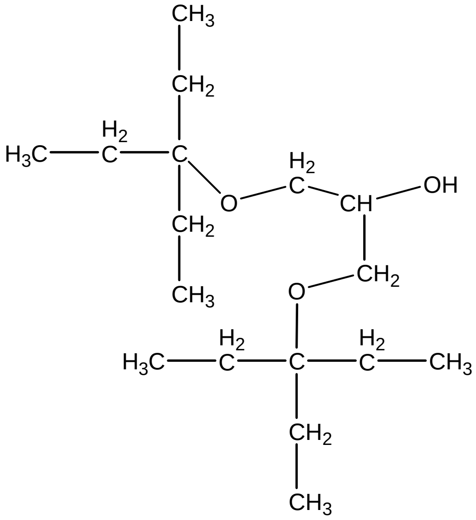
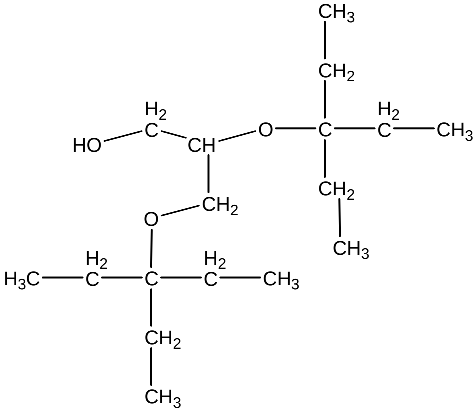
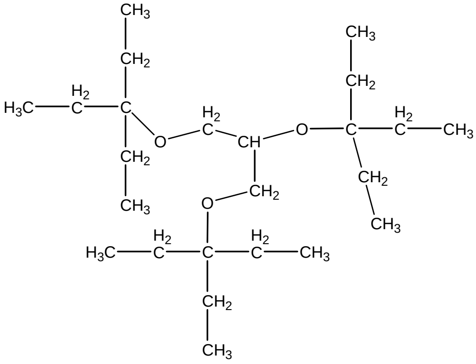
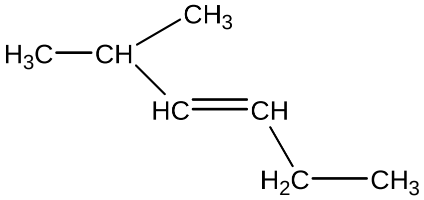
Name	Structure	Sub group
3-(1,1,2-trimethyl-butoxy)-1,2-propanediol		CH_3: 4 CH_2:3 CH: 2 >C<: 1 O: 1 -OH :2
2-(1,1,2-trimethyl-butoxy)-1,3-propanediol		CH_3: 4 CH_2:3 CH: 2 >C<: 1 O: 1 -OH :2
1,3-bis(1,1,2-trimethyl-butoxy)-2-propanol		CH_3: 8 CH_2:4 CH: 3 >C<: 2 O: 2 -OH :1
2,3-bis(1,1,2-trimethyl-butoxy)-1-propanol		CH_3: 8 CH_2:4 CH: 3 >C<: 2 O: 2 -OH :1

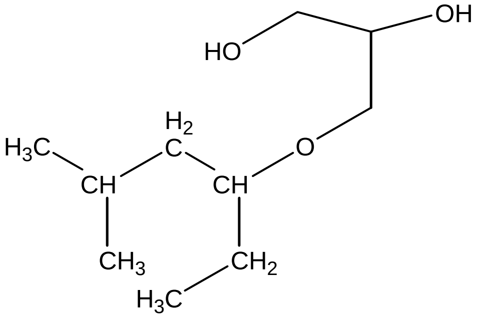
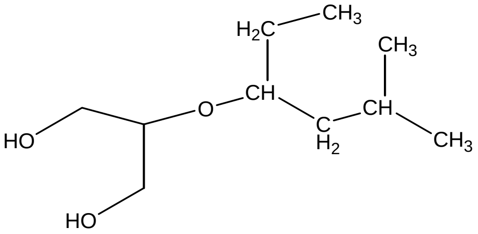
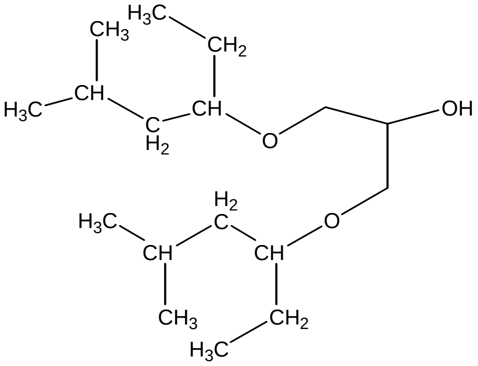
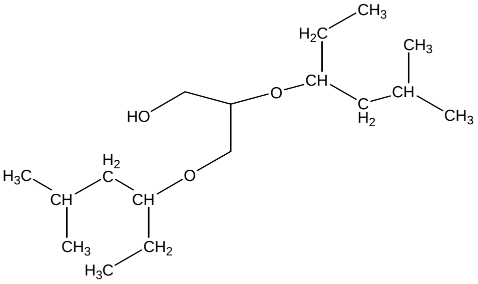
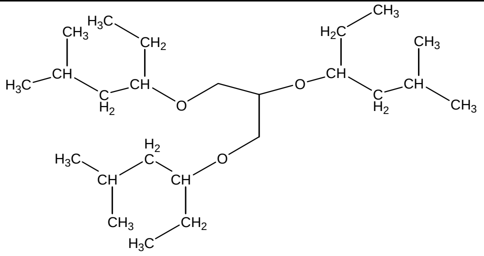
Name	Structure	Sub group
1,2,3-tris(1,1,2-trimethyl-butoxy)- propane		CH_3: 12 CH_2:5 CH: 4 >C<: 3 O: 3
cis-3,4-dimethyl-2-pentene		CH3: 4 >CH- : 1 =CH : 1 =C< : 1
2-ethyl-3-methyl-1-butene		CH3: 3 >CH2 :1 >CH- : 1 =CH2 : 1 =C< : 1
3-(1-methyl-1-isopropyl propoxy)-1,2-propanediol		CH_3: 4 CH_2:3 CH: 2 >C<: 1 O: 1 -OH :2
2-(1-methyl-1-isopropyl propoxy)-1,3-propanediol		CH_3: 4 CH_2:3 CH: 2 >C<: 1 O: 1 -OH :2

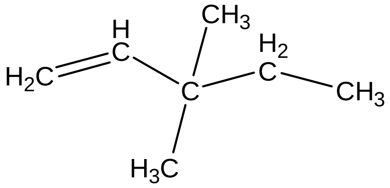
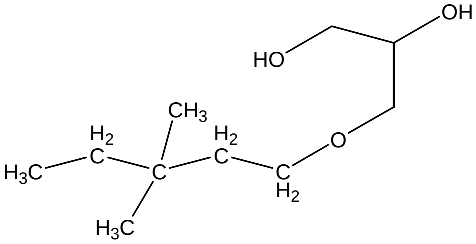
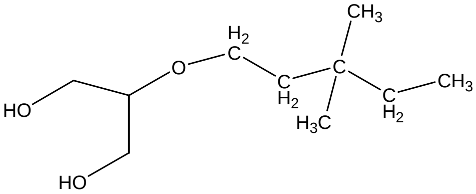
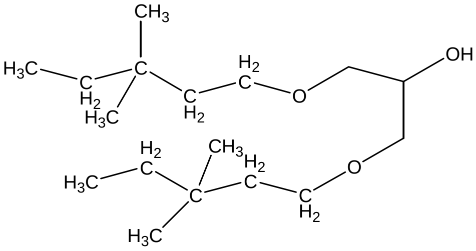
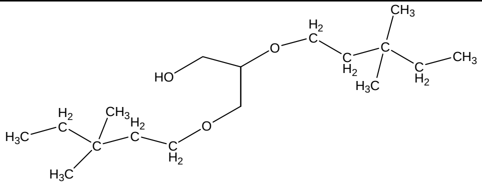
Name	Structure	Sub group
1,3-bis(1-methyl-1-isopropyl propoxy)-2-propanol		CH_3: 8 CH_2:4 CH: 3 >C<: 2 O: 2 -OH :1
2,3-bis(1-methyl-1-isopropyl propoxy)-1-propanol		CH_3: 8 CH_2:4 CH: 3 >C<: 2 O: 2 -OH :1
1,2,3-tris(1-methyl-1-isopropyl propoxy)-propane		CH_3: 12 CH_2:5 CH: 4 >C<: 3 O: 3
2, 4-dimethyl-1-pentene		CH3: 3 >CH2 :1 >CH- : 1 =CH2 : 1 =C< : 1

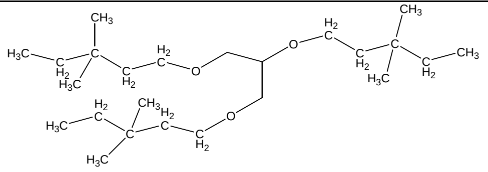
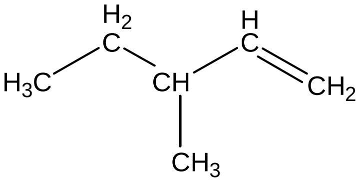
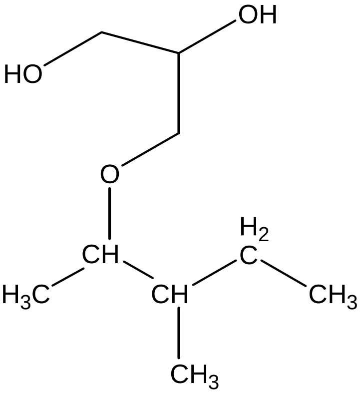
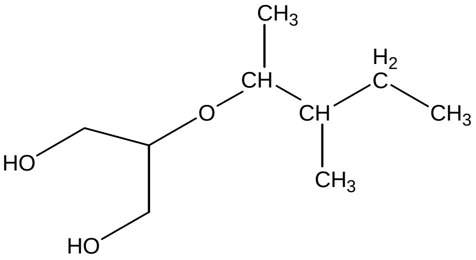
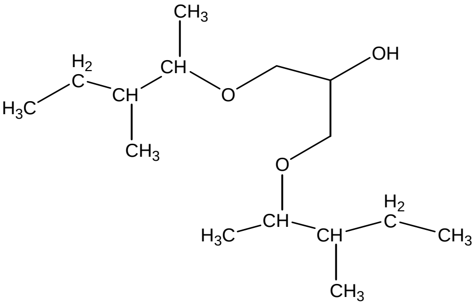
Name	Structure	Sub group
3-(1,1,3-tris methyl butoxy)-1,2-propanediol		CH_3: 4 CH_2:3 CH: 2 >C<: 1 O: 1 -OH :2
2-(1,1,3-tris methyl butoxy)-1,3-propanediol		CH_3: 4 CH_2:3 CH: 2 >C<: 1 O: 1 -OH :2
1,3-bis(1,1,3-tris methyl butoxy)-2-propanol		CH_3: 8 CH_2:4 CH: 3 >C<: 2 O: 2 -OH :1
2,3-bis(1,1,3-tris methyl butoxy)-1-propanol		CH_3: 8 CH_2:4 CH: 3 >C<: 2 O: 2 -OH :1

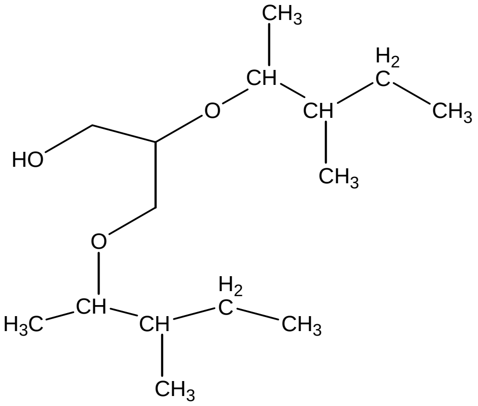
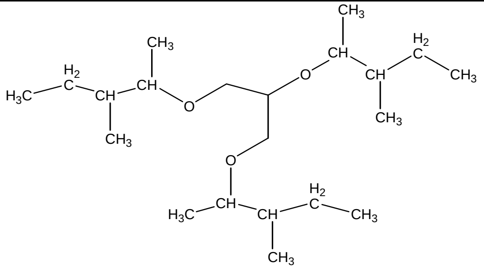
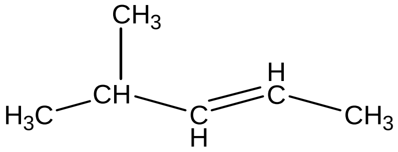
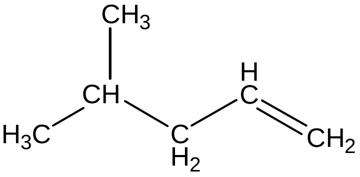
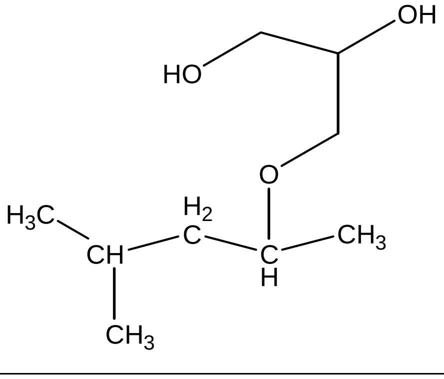
Name	Structure	Sub group
1,2,3-tris(1,1,3-tris methyl butoxy)- propane		CH_3: 12 CH_2:5 CH: 4 >C<: 3 O: 3
3-ethyl-2-pentene		CH3: 3 >CH2 :2 =CH : 1 =C< : 1
3-(1,1-diethyl propoxy)-1,2-propanediol		CH_3: 3 CH_2:5 CH: 1 >C<: 1 O: 1 -OH :2
2-(1,1-diethyl propoxy)-1,3-propanediol		CH_3: 3 CH_2:5 CH: 1 >C<: 1 O: 1 -OH :2

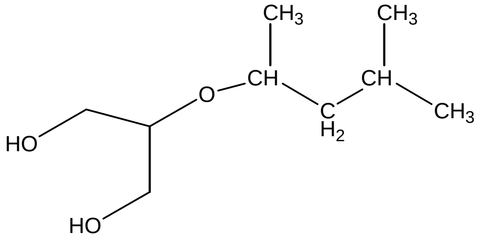
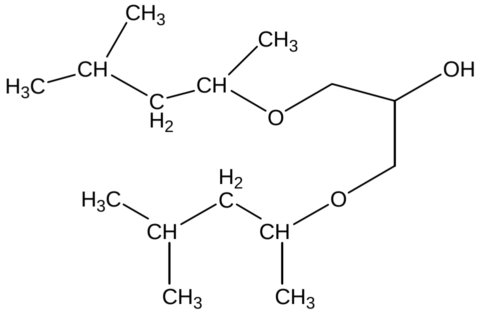
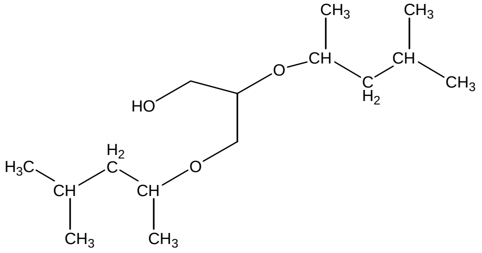
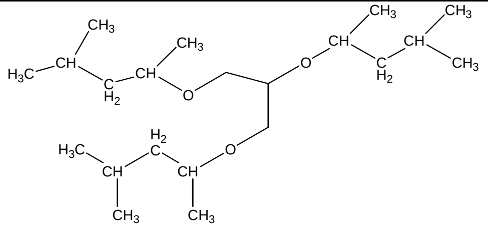
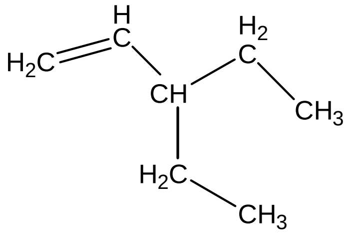
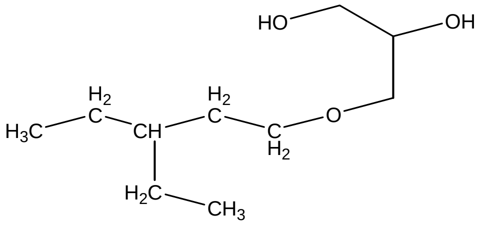
Name	Structure	Sub group
1,3-bis(1,1-diethyl propoxy)-2-propanol		CH_3: 6 CH_2:8 CH: 1 >C<: 2 O: 2 -OH :1
2,3-bis(1,1-diethyl propoxy)-1-propanol		CH_3: 6 CH_2:8 CH: 1 >C<: 2 O: 2 -OH :1
1,2,3-tris(1,1-diethyl propoxy)-propane		CH_3: 9 CH_2:11 CH: 1 >C<: 3 O: 3
Tran-2-methyl-3-hexene		CH3: 3 >CH2 :1 >CH- : 1 =CH : 2

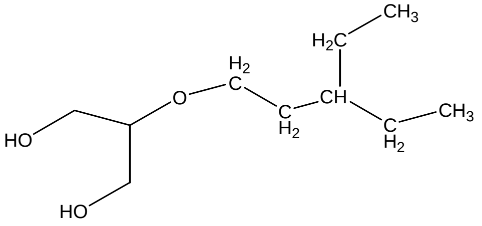
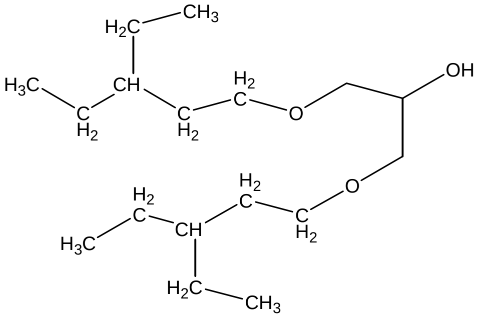
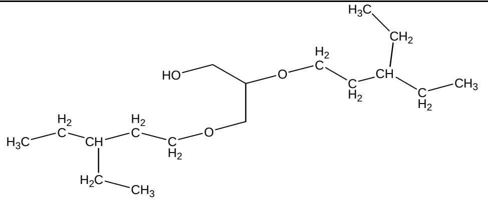
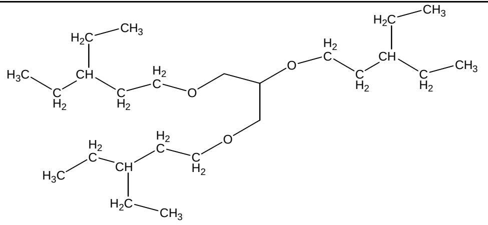
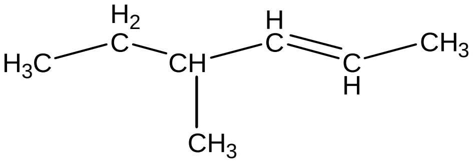
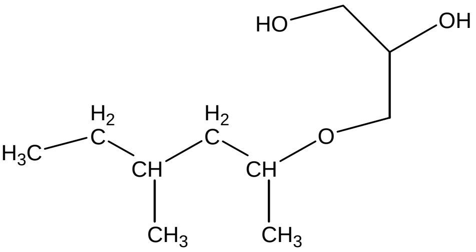
Name	Structure	Sub group
3-(1-ethyl-3-methyl butoxy)-1,2-propanediol		CH_3: 3 CH_2:4 CH: 3 O: 1 -OH :2
2-(1-ethyl-3-methyl butoxy)-1,3-propanediol		CH_3: 3 CH_2:4 CH: 3 O: 1 -OH :2
1,3-bis(1-ethyl-3-methyl butoxy)-2-propanol		CH_3: 6 CH_2:6 CH: 5 O: 2 -OH :1
2,3-bis(1-ethyl-3-methyl butoxy)-1-propanol		CH_3: 6 CH_2:6 CH: 5 O: 2 -OH :1
1,2,3-tris-(1-ethyl-3-methyl butoxy)- propane		CH_3: 9 CH_2:8 CH: 7 O: 3

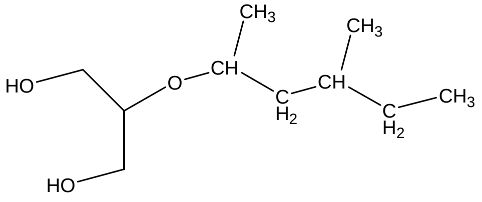
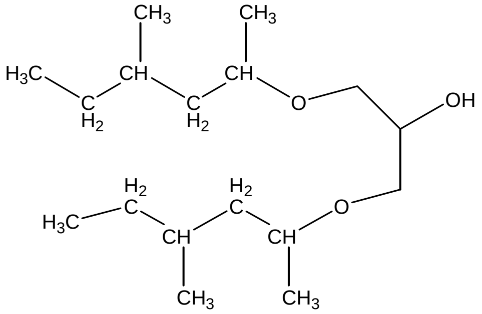
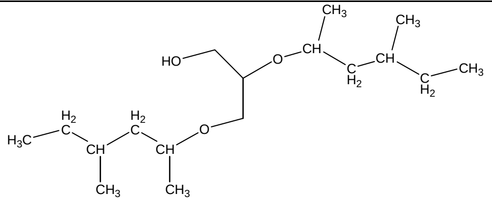
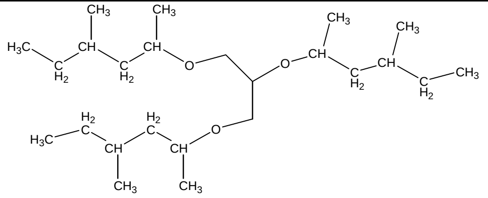
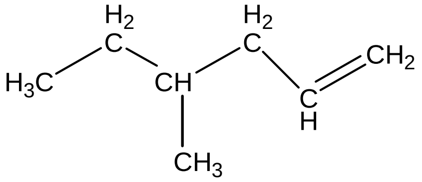
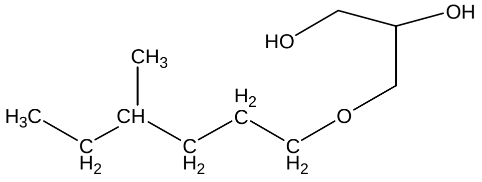
Name	Structure	Sub group
3,3-dimethyl-1-pentene		CH3: 3 >CH2 :1 >C< : 1 =CH2 :1 =CH : 1
3-(1,1-dimethyl pentoxy)-1,2-propanediol		CH_3: 3 CH_2:5 CH: 1 >C<: 1 O: 1 -OH :2
2-(1,1-dimethyl pentoxy)-1,3-propanediol		CH_3: 3 CH_2:5 CH: 1 >C<: 1 O: 1 -OH :2
1,3-bis(1,1-dimethyl pentoxy)-2-propanol		CH_3: 6 CH_2:8 CH: 1 >C<: 2 O: 2 -OH :1
2,3-bis(1,1-dimethyl pentoxy)-1-propanol		CH_3: 6 CH_2:8 CH: 1 >C<: 2 O: 2 -OH :1

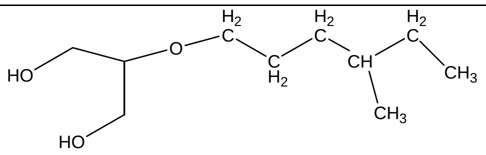
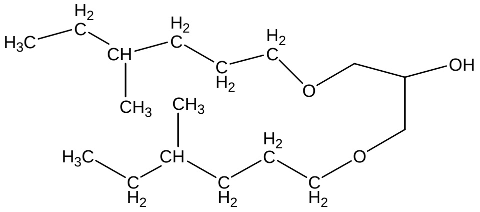
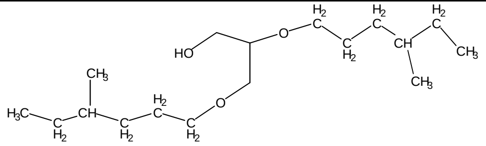
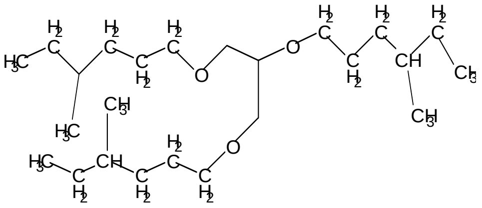
Name	Structure	Sub group
1,2,3-tris-(1,1-dimethyl pentoxy)- propane		CH_3: 9 CH_2:11 CH: 1 >C<: 3 O: 3
3-methyl-1-pentene		CH3: 2 >CH2 :1 >C< : 1 =CH2 :1 =CH : 1
3- (3-ethyl -pentoxy)-1,2-propanediol		CH_3: 3 CH_2:3 CH: 3 O: 1 -OH :2
2 -(3-ethyl -pentoxy)-1,3-propanediol		CH_3: 3 CH_2:3 CH: 3 O: 1 -OH :2
1,3-bis(3-ethyl-pentoxy)-2-propanol		CH_3: 6 CH_2:4 CH: 5 O: 2 -OH :1

Name	Structure	Sub group
2,3-bis(3-ethyl- pentoxy)-1-propanol		CH_3: 6 CH_2:4 CH: 5 O: 2 -OH :1
1,2,3-tris-(3-ethyl- pentoxy)-propane		CH_3: 9 CH_2:5 CH: 7 O: 3
Cis-4-methyl-2-pentene		CH3: 3 >CH : 1 =CH : 2
4-methyl-1-pentene		CH3: 2 >CH2 :1 >CH : 1 =CH2 :1 =CH : 1
3 -(1,4-dimethyl -butoxy)-1,2-propanediol		CH_3: 3 CH_2:3 CH: 3 O: 1 -OH :2

Name	Structure	Sub group
2 -(1,4-dimethyl -butoxy)-1,3-propanediol		CH_3: 3 CH_2:3 CH: 3 O: 1 -OH :2
1,3-bis(1,4-dimethyl- butoxy)-2-propanol		CH_3: 6 CH_2:4 CH: 5 O: 2 -OH :1
2,3-bis(1,4-dimethyl- butoxy)-1-propanol		CH_3: 6 CH_2:4 CH: 5 O: 2 -OH :1
1,2,3-tris-(1,4-dimethyl-butoxy)- propane		CH_3: 9 CH_2:5 CH: 7 O: 3
3-ethyl-1-pentene		CH3: 2 >CH2 :2 >CH : 1 =CH2 :1 =CH : 1
3-(1-methyl-2-ethyl-butoxy)-1,2-propanediol		CH_3: 2 CH_2:6 CH: 2 O: 1 -OH :2

Name	Structure	Sub group
2-(1-methyl-2-ethyl-butoxy)-1,3-propanediol		CH_3: 2 CH_2:6 CH: 2 O: 1 -OH :2
1,3-bis(1-methyl-2-ethyl-butoxy)-2-propanol		CH_3: 4 CH_2:10 CH: 3 O: 2 -OH :1
2,3-bis(1-methyl-2-ethyl-butoxy)-1-propanol		CH_3: 4 CH_2:10 CH: 3 O: 2 -OH :1
1,2,3-tris-(1-methyl-2-ethyl-butoxy)- propane		CH_3: 6 CH_2:14 CH: 4 O: 3
Cis-5-methyl-2-hexene		CH3: 3 >CH2 :1 >CH : 1 =CH : 2
3-(1,3-dimethyl-pentoxy)-1,2-propanediol		CH_3: 3 CH_2:4 CH: 3 O: 1 -OH :2

Name	Structure	Sub group
2-(1,3-dimethyl-pentoxy)-1,3-propanediol		CH_3: 3 CH_2:4 CH: 3 O: 1 -OH :2
1,3-bis(1,3-dimethyl-pentoxy)-2-propanol		CH_3: 6 CH_2:6 CH: 5 O: 2 -OH :1
2,3-bis(1,3-dimethyl-pentoxy)-1-propanol		CH_3: 6 CH_2:6 CH: 5 O: 2 -OH :1
1,2,3-tris-(1,3-dimethyl-pentoxy)- propane		CH_3: 9 CH_2:8 CH: 7 O: 3
4-methyl-1-hexene		CH3: 2 >CH2 :2 >CH : 1 =CH : 1 =CH2 :1
3-(4-methyl-hexoxy)-1,2-propanediol		CH_3: 2 CH_2:6 CH: 2 O: 1 -OH :2

Name	Structure	Sub group
2-(4-methyl-hexoxy)-1,3-propanediol		CH_3: 2 CH_2:6 CH: 2 O: 1 -OH :2
1,3-bis(4-methyl-hexoxy)-2-propanol		CH_3: 4 CH_2:10 CH: 3 O: 2 -OH :1
2,3-bis(4-methyl-hexoxy)-1-propanol		CH_3: 4 CH_2:10 CH: 3 O: 2 -OH :1
1,2,3-tris-(4-methyl-hexoxy)-propane		CH_3: 6 CH_2:14 CH: 4 O: 3

Note: Joback's subgroup (Aspen subgroup ID) will be listed below;

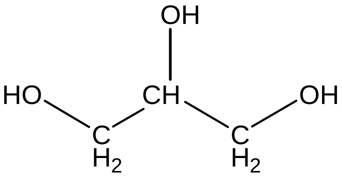
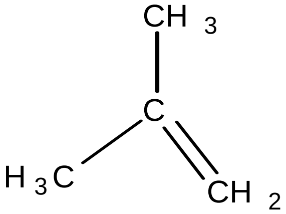
-CH3 (100), >CH2 (101), >CH- (102), >C< (103), =CH2 (104), >CH2 ring increments (110), >CH- ring increment (111), =C< ring increment (114), -O- non-ring (122), -OH alcohols (119).

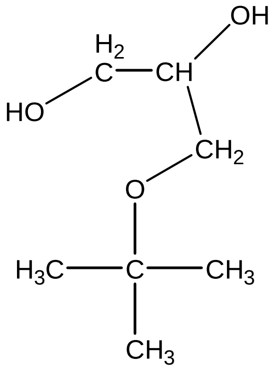
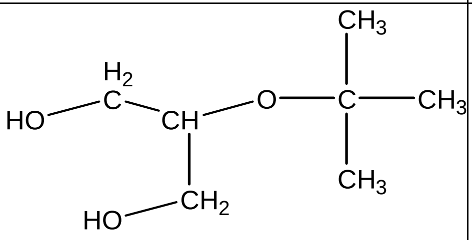
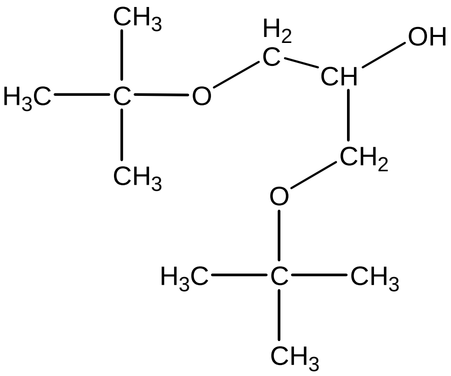
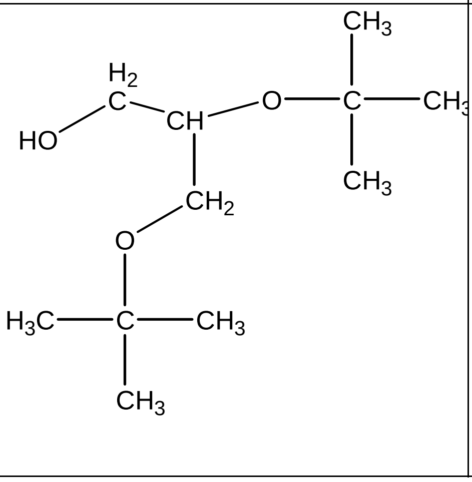
APPENDIX B

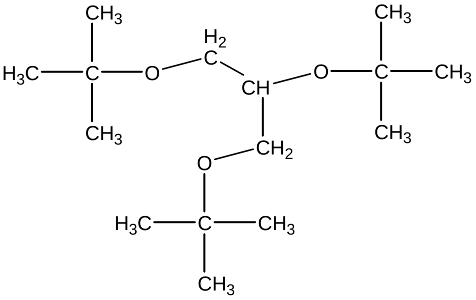
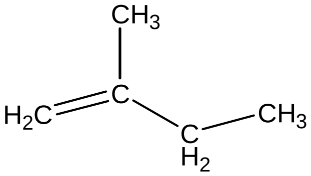
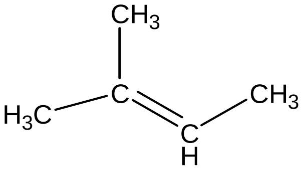
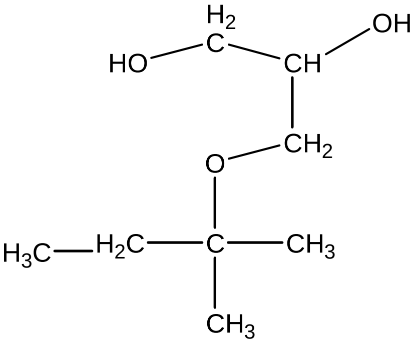
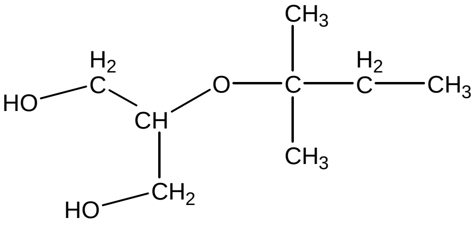
GANI'S GROUP CONTRIBUTION METHOD

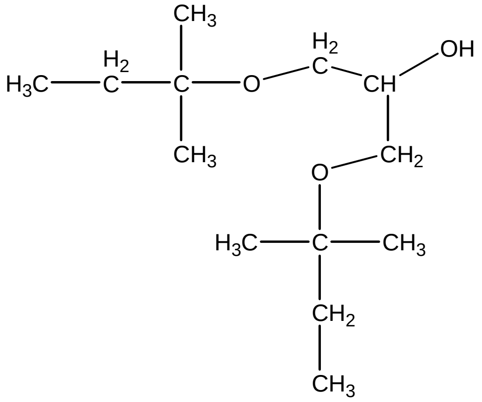
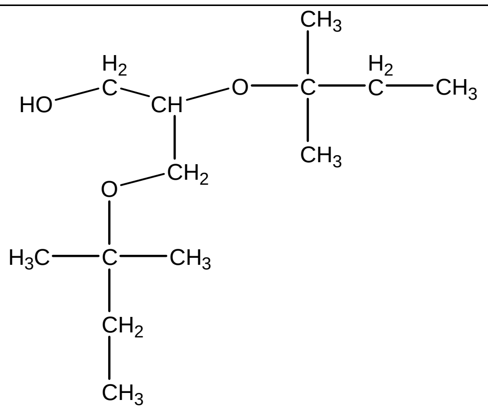
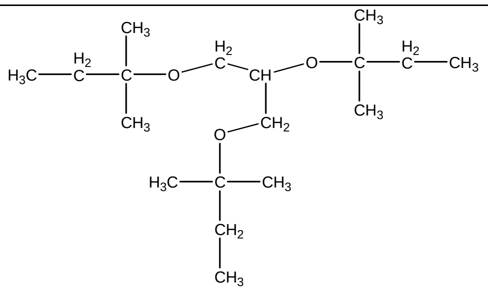
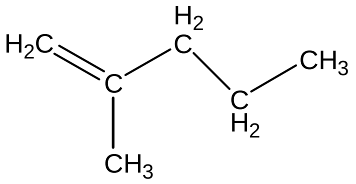
The functional groups of components in olefins are listed below with the number of subgroup in each component. Gani's group contribution method will be used to estimate the property of olefin components. This method can be used to estimate critical properties such as critical temperature and critical pressure or normal boiling point or estimated the thermodynamic properties such as Gibbs of formation.

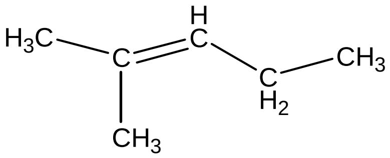
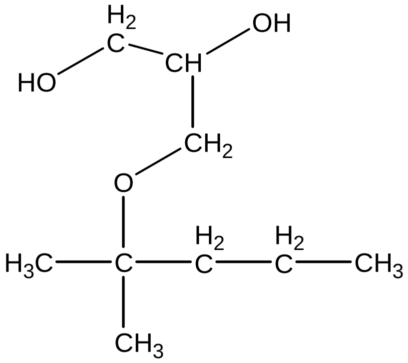
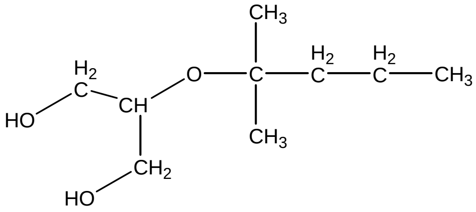
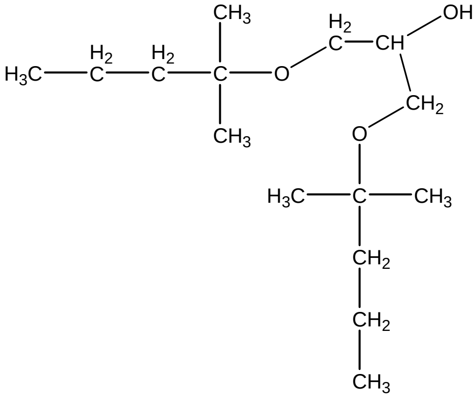
Table B. Sub group of components

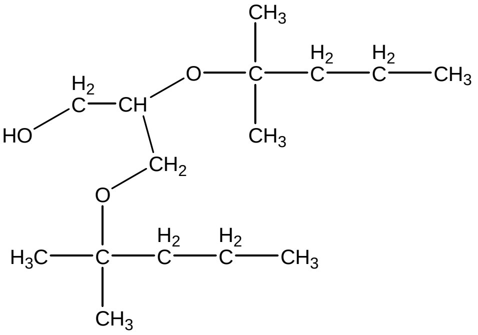
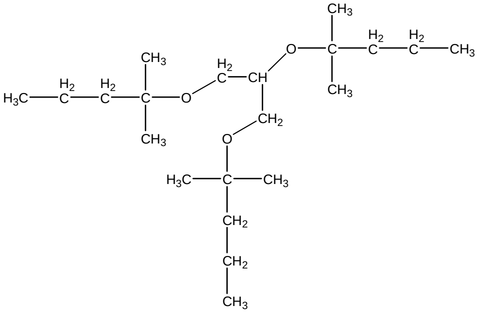
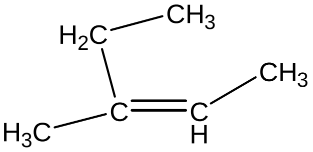
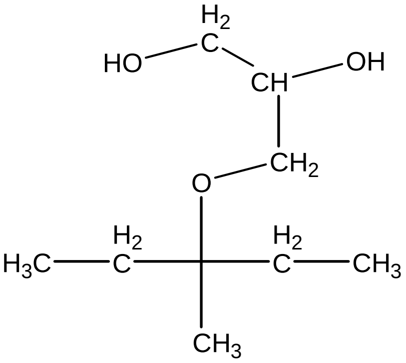
Name	Structure	Sub group
Glycerol		$>CH_2$:2 >CH-: 1 -OH: 3
Isobutene		$-CH_3$: 2 $>C=CH_2$: 2

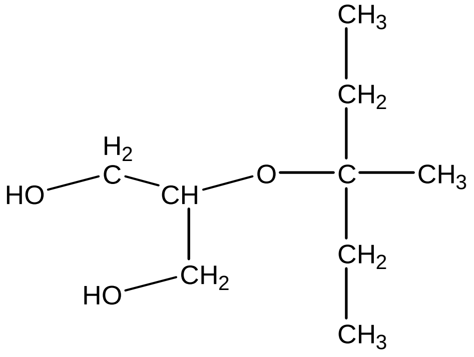
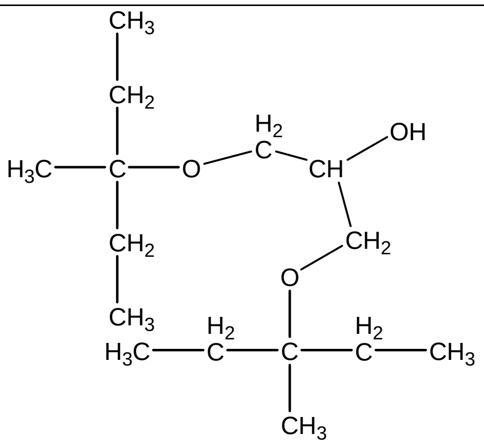
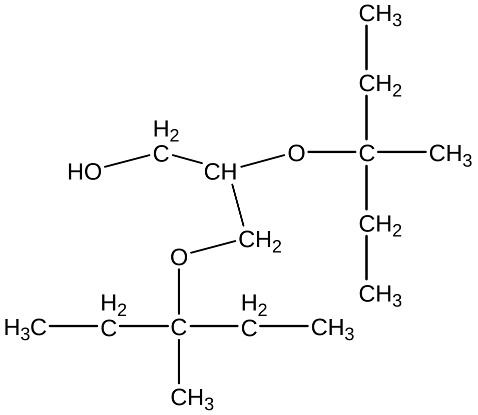
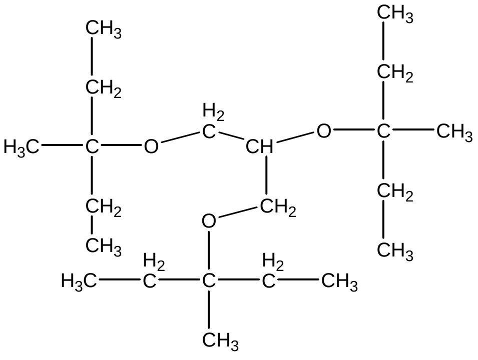
Name	Structure	Sub group
3-tert-butoxy -1,2-propanediol		$-CH_3$: 3 $>CH_2$: 2 >CH-: 1 >C< : 1 -OH : 2 -CH2-O-(C) : 1 (CH3)3C: 1 CH2(OH)CH(OH):1
2-tert-butoxy -1,3-propanediol		$-CH_3$: 3 $>CH_2$: 2 >CH-: 1 >C< : 1 -OH : 2 -CH2-O-(C) : 1 (CH3)3C: 1
1,3-di-tert-butoxy-2-propanol		$-CH_3$: 6 $>CH_2$: 2 >CH-: 1 >C< : 2 -CH2-O-(C) : 2 (CH3)3C: 2 CHOH : 1 OH :1
2,3-di-tert-butoxy-1-propanol		$-CH_3$: 6 $>CH_2$: 2 >CH-: 1 >C< : 2 -CH2-O-(C) : 1 (CH3)3C: 2 >CH-O-(C) : 1

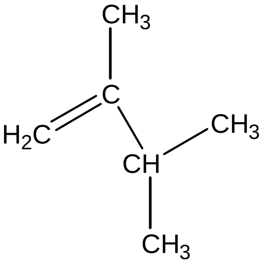
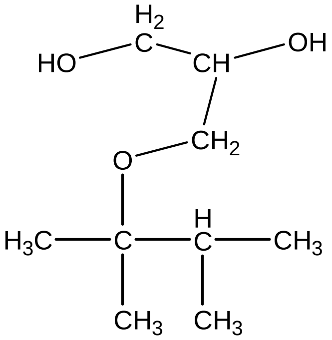
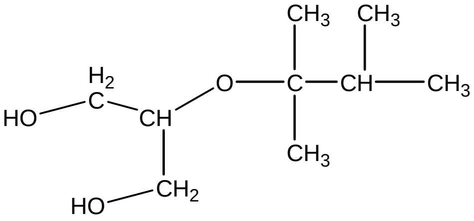
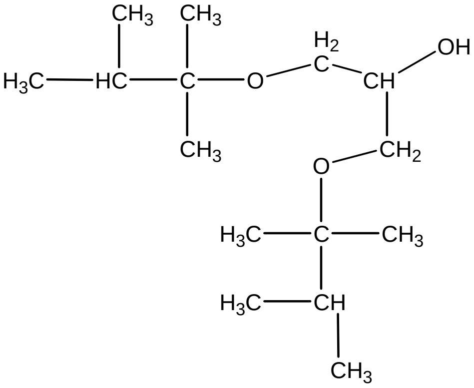
Name	Structure	Sub group
1,2,3- tri-tert-butoxy-propane		CH_3 : 9 >CH_2 : 2 >CH-: 1 >C< : 3 -CH2-O-(C) : 2 (CH3)3C: 3 >CH-O-(C) :1
2-methyl-1-butene		CH_3 : 2 >CH_2 : 1 >C=CH2: 1 CH3-C=CH2:1
2-methyl-2-butene		CH_3 : 3 -CH=C< : 1 CH3-C=CH : 1
3(1,1-dimethyl-propoxy)-1,2-propanediol		CH_3 : 3 >CH_2 : 3 >CH-: 1 >C< : 1 -OH : 2 -CH2-O-(C) : 1 (CH3)3C: 1 CH2(OH)CH(OH): 1>CH_2 : 1
2(1,1-dimethyl-propoxy)-1,3-propanediol		CH_3 : 3 >CH_2 : 3 >CH-: 1 >C< : 1 -OH : 2 -CH2-O-(C) : 1 (CH3)3C: 1

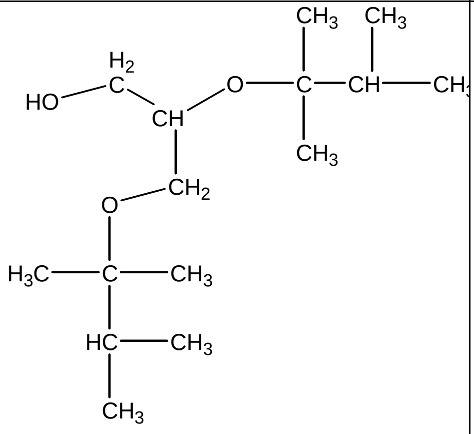
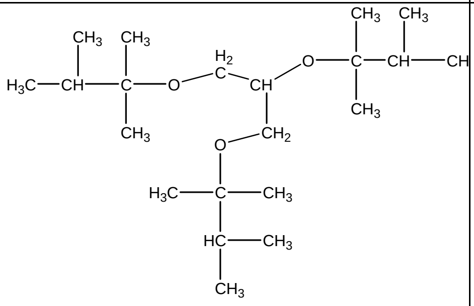
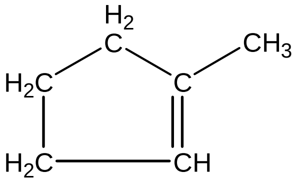
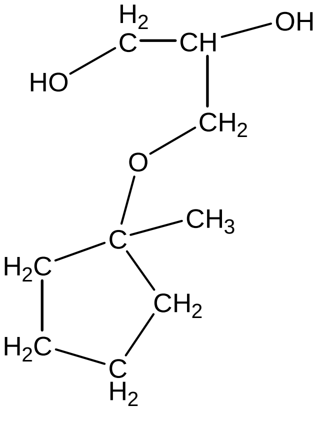
Name	Structure	Sub group
1,3-bis-(1,1-dimethyl propoxy) -2-propanol		CH_3 : 6 >CH_2 : 4 >CH-: 1 >C< : 2 -OH : 1 -CH2-O-(C) : 2 (CH3)3C: 2 CHOH :1
2,3-bis-(1,1-dimethyl propoxy) -1-propanol		CH_3 : 6 >CH_2 : 4 >CH-: 1 >C< : 2 -OH : 1 -CH2-O-(C) : 2 (CH3)3C: 2 >CH-O-(C) : 1
1,2,3-tris-(1,1-dimethyl propoxy)-propane		CH_3 : 9 >CH_2 : 5 >CH-: 1 >C< : 3 -CH2-O-(C) : 2 (CH3)3C: 3 >CH-O-(C) : 1
2-methyl-1-pentene		CH_3 : 2 >CH_2 : 2 >C=CH2 : 2 CH3-C=CH2 : 1 CH2-C=CH2: 1
Name	Structure	Sub group

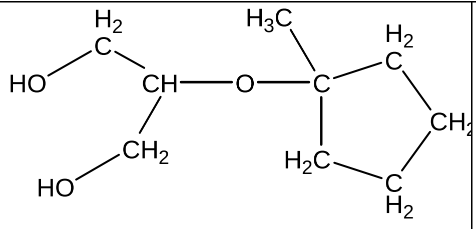
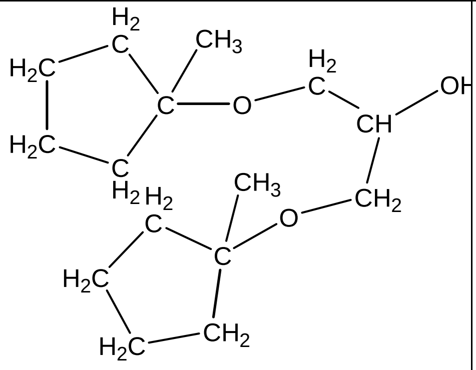
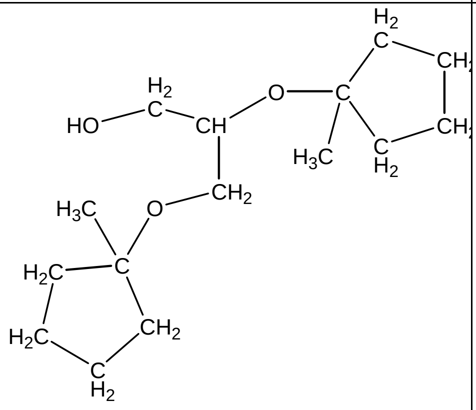
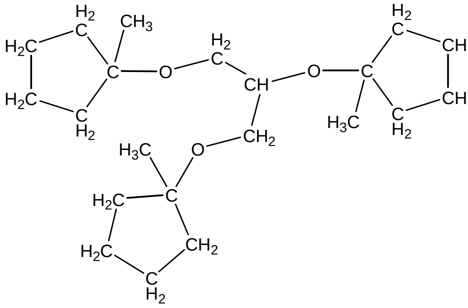
2-methyl-2-pentene		CH_3 : 2 >CH_2 : 2 -CH=C< : 2 CH3-C=CH : 1
3-(1,1-dimethyl butoxy)-1,2-propanediol		CH_3 : 3 >CH_2 : 4 >CH-: 1 >C< : 1 -OH : 2 -CH2-O-(C) : 1 (CH3)3C: 1 CH2(OH)CH(OH): 1>CH_2 : 1
2-(1,1-dimethyl butoxy)-1,3-propanediol		CH_3 : 3 >CH_2 : 4 >CH-: 1 >C< : 1 -OH : 2 -CH2-O-(C) : 1 (CH3)3C: 1
1,3-bis (1,1-dimethyl butoxy)-2-propanol		CH_3 : 6 >CH_2 : 6 >CH-: 1 >C< : 2 -OH : 1 -CH2-O-(C) : 2 (CH3)3C: 2 CHOH :1

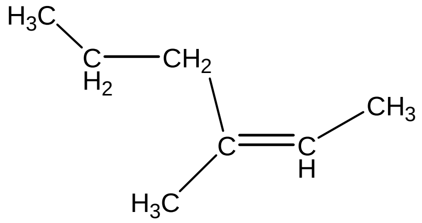
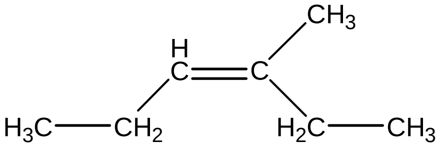
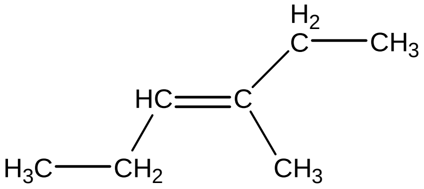
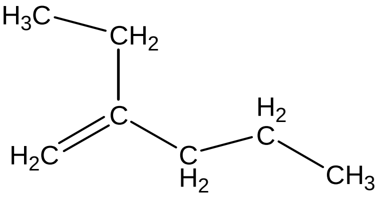
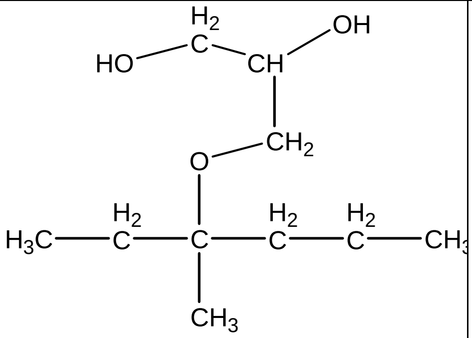
Name	Structure	Sub group
2,3-bis (1,1-dimethyl butoxy)-1-propanol		CH_3 : 6 >CH_2 : 6 >CH-: 1 >C< : 2 -OH : 1 -CH2-O-(C) : 1 (CH3)3C: 2
1,2,3-tris(1,1-dimethyl butoxy)-propane		CH_3 : 9 >CH_2 : 8 >CH-: 1 >C< : 3 -CH2-O-(C) : 2 (CH3)3C: 3 >CH-O-(C) : 1
cis-3-methyl-2-pentene		CH_3 : 3 >CH_2 : 1 -CH=C< : 2 CH3-C=CH : 1 CH3-CH=C : 1
3-(1-methyl-2-ethyl-propoxy)-1,2-propanediol		CH_3 : 3 >CH_2 : 4 >CH-: 1 >C< : 1 -OH : 2 >CH-O-(C) : 1 (CH3)3C : 1 CH2(OH)CH(OH): 1

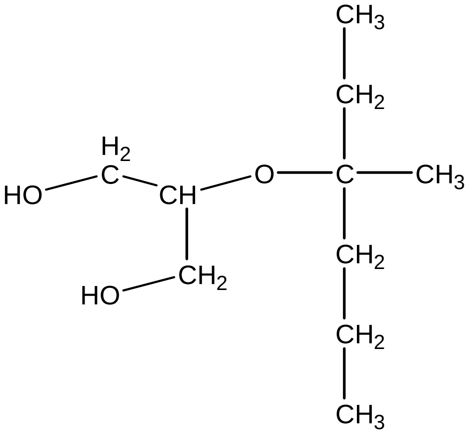
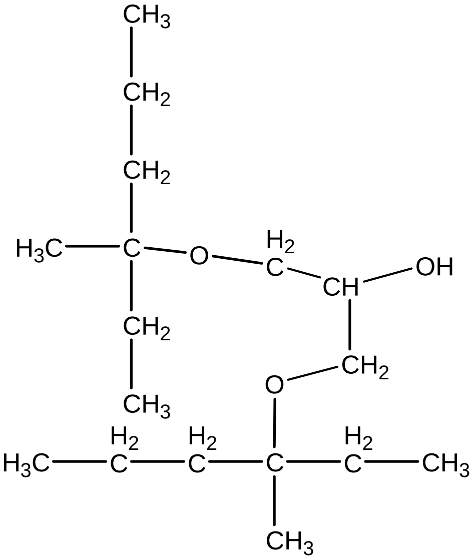
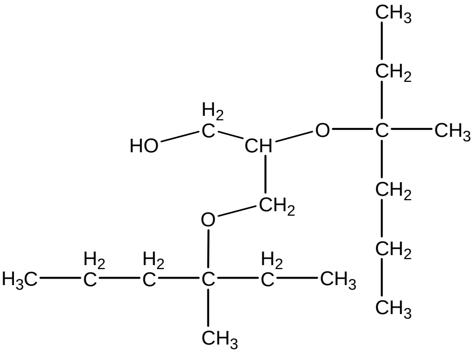
Name	Structure	Sub group
2-(1-methyl-2-ethyl-propoxy)-1,3-propanediol		CH_3 : 3 >CH_2 : 4 >CH-: 1 >C< : 1 -OH : 2 >CH-O-(C) : 1 (CH3)3C : 1
1,3-bis (1,1-methyl-2-ethyl-propoxy)-2- propanol		CH_3 : 6 >CH_2 : 6 >CH-: 1 >C< : 2 -OH : 1 -CH2-O-(C) : 2 (CH3)3C: 2 CHOH :1
2,3-bis (1,1-methyl-2-ethyl -propoxy)-1- propanol		CH_3 : 6 >CH_2 : 6 >CH-: 1 >C< : 2 -OH : 1 -CH2-O-(C) : 1 (CH3)3C: 2 >CH-O-(C) : 1
1,2,3-tris (1-methyl-2-ethyl-propoxy)- propane		CH_3 : 9 >CH_2 : 8 >CH-: 1 >C< : 3 -CH2-O-(C) : 2 (CH3)3C: 3 >CH-O-(C) : 1

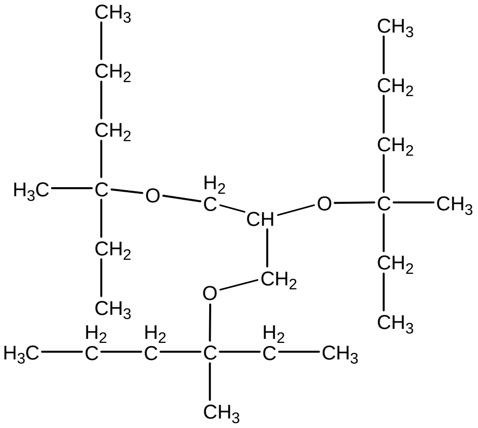
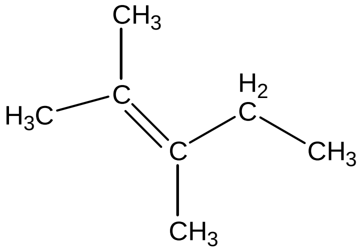
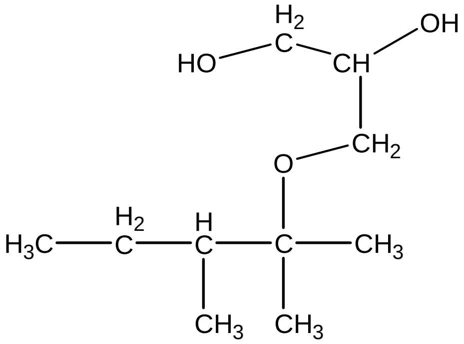
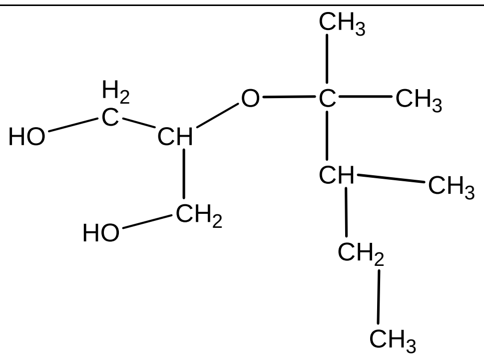
Name	Structure	Sub group
2,3-dimethyl-1-butene		CH_3 : 3 >CH_{-} : 1 >C=CH2 : 2 (CH3)2CH:1 CH2-C=CH:1
3-(1,1,2-trimethyl-propoxy)-1,2-propanediol		CH_3 : 4 >CH_2 : 2 >CH-: 2 >C< : 1 -OH : 2 (CH3)3C : 1 CH2(OH)CH(OH):1
2-(1,1,2-trimethyl-propoxy)-1,3-propanediol		CH_3 : 4 >CH_2 : 2 >CH-: 2 >C< : 1 -OH : 2 >CH-O-(C) : 1 (CH3)3C : 1
1,3-bis(1,1,2-trimethyl-propoxy)-2-propanol		CH_3 : 8 >CH_2 : 3 >CH-: 3 >C< : 2 -OH : 1 -CH2-O-(C) : 2 (CH3)3C: 2 CHOH :1

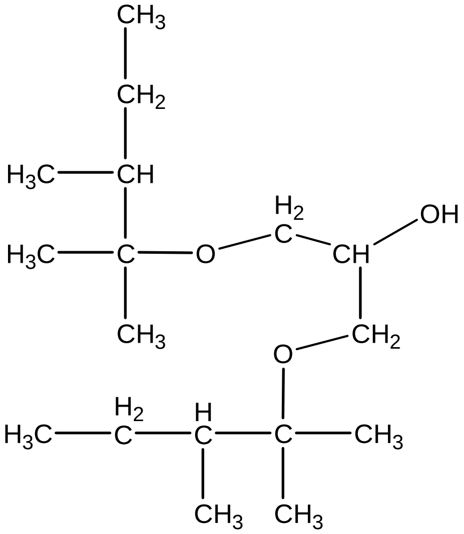
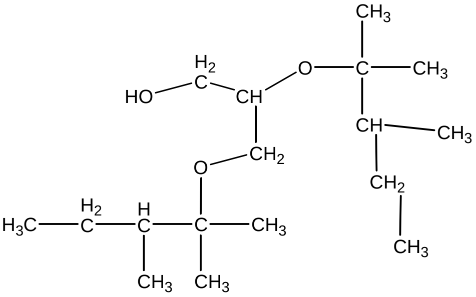
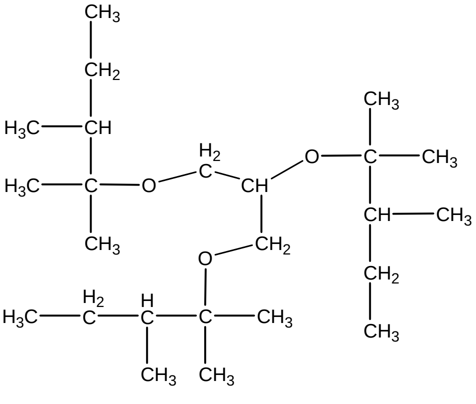
Name	Structure	Sub group
2,3-bis(1,1,2-trimethyl-propoxy)-1-propanol		CH_3 : 8 $>CH_2$: 2 >CH-: 2 >C< : 2 -OH : 1 -CH2-O-(C) : 1 (CH3)3C: 1
1,2,3-tris(1,1,2-trimethyl-propoxy)-propane		CH_3 : 12 $>CH_2$: 2 >CH-: 4 >C< : 3 -CH2-O-(C) : 2 (CH3)3C: 3
1-methylcyclopentene		-CH3 : 1 >CH2 : 3 -CH=C< : 2 CH3-C=CH :1
3-(1,1,2-trimethyl-propoxy)-1,2-propanediol		$-CH_3$: 1 $>CH_2$: 6 >CH-: 1 >C< : 1 -OH : 2 -CH2-O-(C) : 1 (CH3)3C: 1 CH2(OH)CH(OH):1

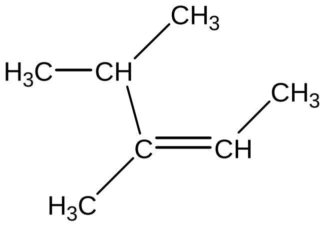
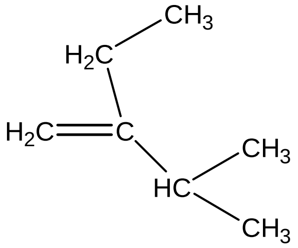
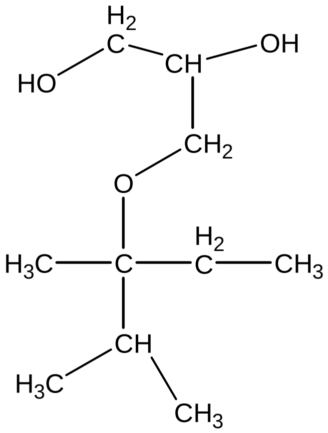
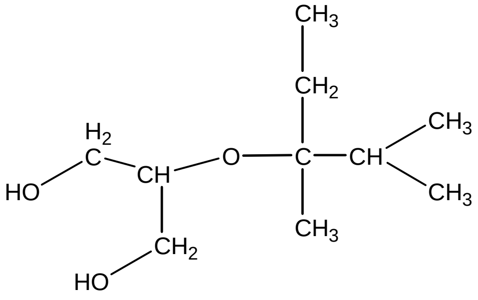
2-(1,1,2-trimethyl-propoxy)-1,3-propanediol		-CH_3 : 1 >CH_2 : 6 >CH-: 1 >C< : 1 -OH : 2 -CH2-O-(C) : 1 (CH3)3C: 1
1,3-bis-(1-methyl cyclopentyloxy)-2-propanol		-CH_3 : 2 >CH_2 : 10 >CH-: 1 >C< : 2 -CH2-O-(C) : 2 (CH3)3C: 2 CHOH : 1 OH :1
2,3-bis-(1-methyl cyclopentyloxy)-1-propanol		-CH_3 : 2 >CH_2 : 10 >CH-: 1 >C< : 2 -CH2-O-(C) : 1 (CH3)3C: 2 >CH-O-(C) : 1 OH :1
1,2,3-tris(1-methyl cylopentyloxy)-propane		-CH_3 : 3 >CH_2 : 14 >CH-: 1 >C< : 3 -CH2-O-(C) : 1 (CH3)3C: 2 >CH-O-(C) : 1

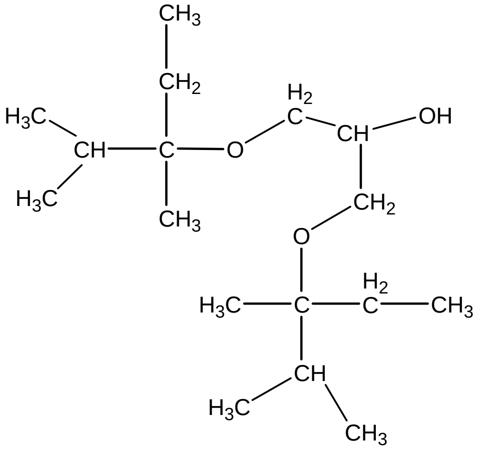
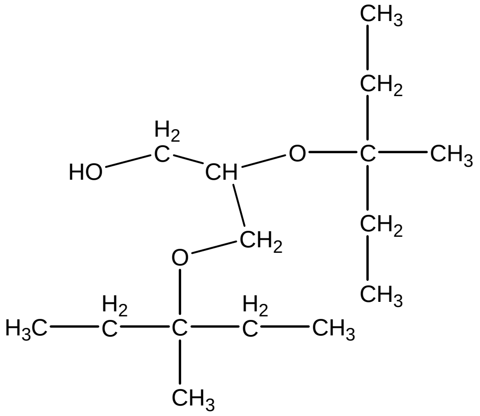
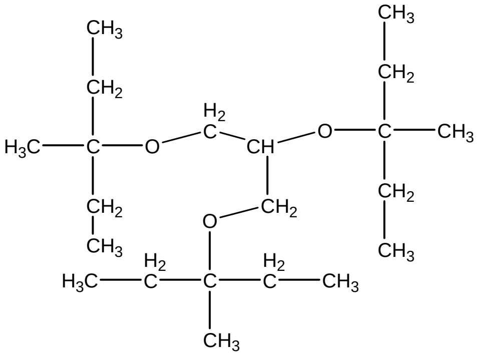
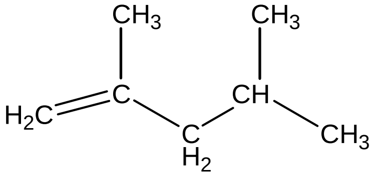
cis-methyl-2-hexene		-CH_3 : 3 >CH_2 : 2 -CH=C< : 2 CH2-CH=C : 1 CH2-C=CH : 1
cis-3-methyl-3-hexene		-CH_3 : 3 >CH_2 : 2 -CH=C< : 2 CH2-CH=C : 1 CH2-C=CH : 1
trans-3-methyl-3-hexene		-CH_3 : 3 >CH_2 : 2 -CH=C< : 2 CH2-CH=C : 1 CH2-C=CH : 1
2-ethyl-1-pentene		-CH_3 : 3 >CH_2 : 2 >C=CH2 : 2 CH2-C=CH2: 1
3-(1-methyl-1-ethyl-butoxy)-1,2-propanediol		-CH_3 : 3 >CH_2 : 5 >CH-: 1 >C< : 1 -OH : 2 -CH2-O-(C) : 1 (CH3)3C: 1 CH2(OH)CH(OH):1

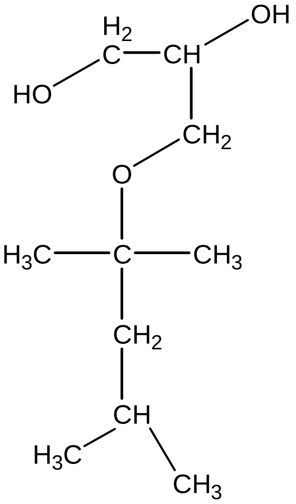
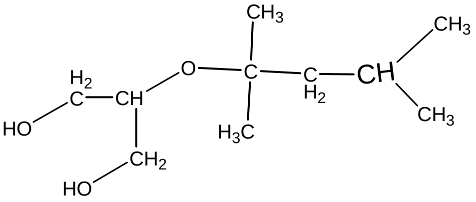
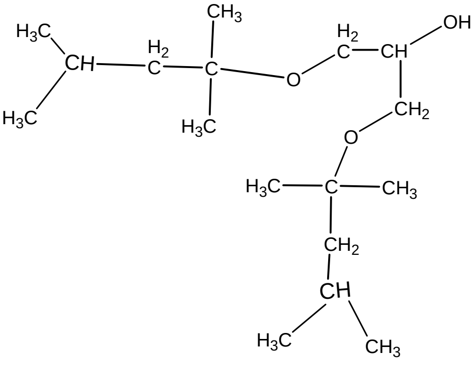
Name	Structure	Sub group
2-(1-methyl-1-ethyl-butoxy)-1,3-propanediol		-CH$_3$: 3 >CH$_2$: 5 >CH-: 1 >C< : 1 -OH : 2 -CH2-O-(C) : 1 (CH3)3C: 1 >CH-O-(C) : 1
1,3-bis(1-methyl-1-ethyl-butoxy)-2-propanol		-CH$_3$: 6 >CH$_2$: 8 >CH-: 1 >C< : 2 -OH : 1 -CH2-O-(C) : 2 (CH3)3C: 1
2,3-bis(1-methyl-1-ethyl-butoxy)-1-propanol		-CH$_3$: 6 >CH$_2$: 8 >CH-: 1 >C< : 2 -OH : 1 -CH2-O-(C) : 2 (CH3)3C: 1 >CH-O-(C) : 1

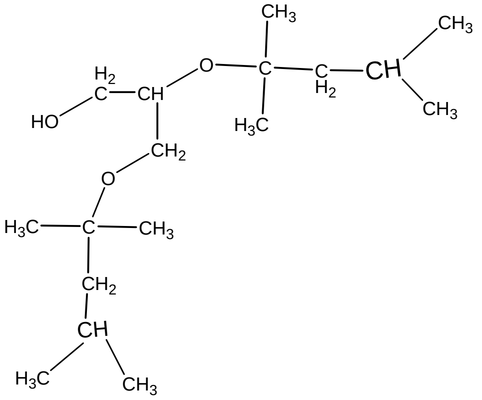
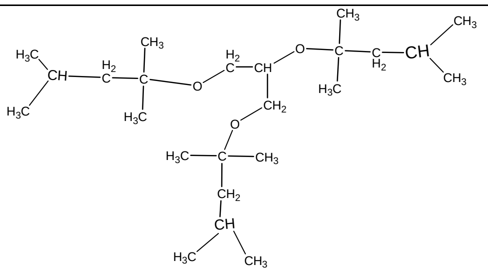
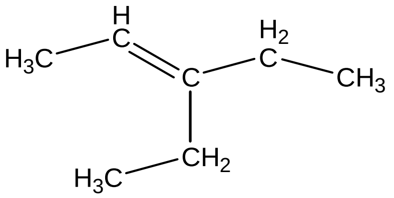
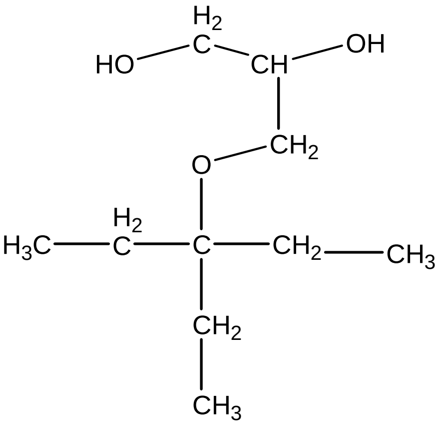
Name	Structure	Sub group
1,2,3-tris(1-methyl-1-ethyl-butoxy)- propane		-CH$_3$: 9 >CH$_2$: 11 >CH-: 1 >C< : 3 -CH2-O-(C) : 2 >CH-O-(C) : 1
2, 3-dimethyl-2-pentene		-CH$_3$: 4 >CH$_2$: 1 >C=C< : 2 CH3-C=C : 1 CH2-C=C : 1
3-(1,1,2-trimethyl-butoxy)-1,2-propanediol		-CH$_3$: 4 >CH$_2$: 3 >CH-: 2 >C< : 1 -OH : 2 (CH3)3C: 1 >CH-O-(C) : 1 CH2(OH)CH(OH) : 1
2-(1,1,2-trimethyl-butoxy)-1,3-propanediol		-CH$_3$: 4 >CH$_2$: 3 >CH-: 2 >C< : 1 -OH : 2 (CH3)3C: 1 >CH-O-(C) : 1

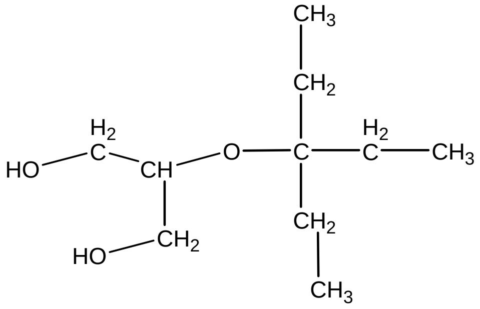
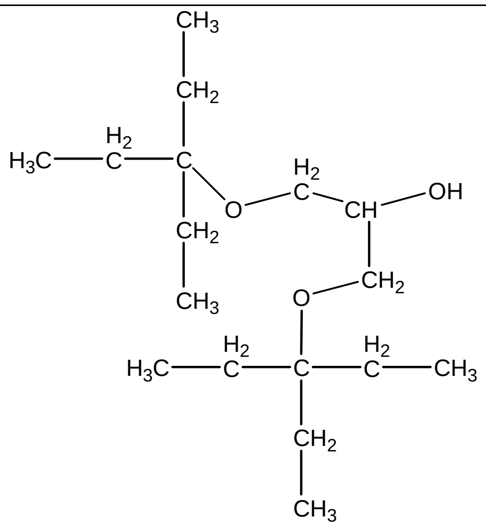
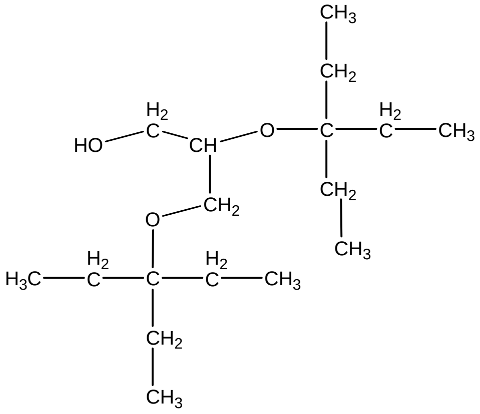
Name	Structure	Sub group
1,3-bis(1,1,2-trimethyl-butoxy)-2-propanol		$-CH_3$: 8 $>CH_2$: 4 >CH-: 3 >C< : 2 -OH : 1 (CH3)3C: 2 -CH2-O-(C) : 1
2,3-bis(1,1,2-trimethyl-butoxy)-1-propanol		$-CH_3$: 8 $>CH_2$: 4 >CH-: 3 >C< : 2 -OH : 1 (CH3)3C: 2 >CH-O-(C) : 1 -CH2-O-(C) : 1
1,2,3-tris(1,1,2-trimethyl-butoxy)- propane		$-CH_3$: 12 $>CH_2$: 5 >CH-: 4 >C< : 3 (CH3)3C: 3 >CH-O-(C) : 1 -CH2-O-(C) : 1

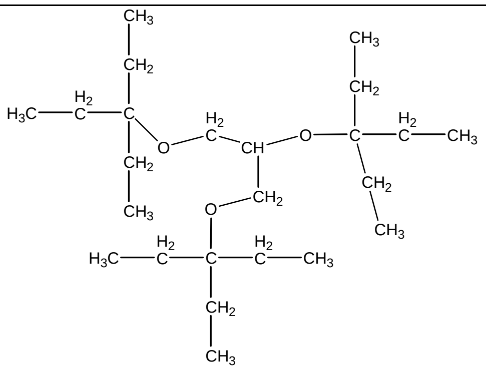
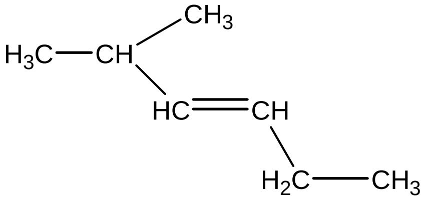
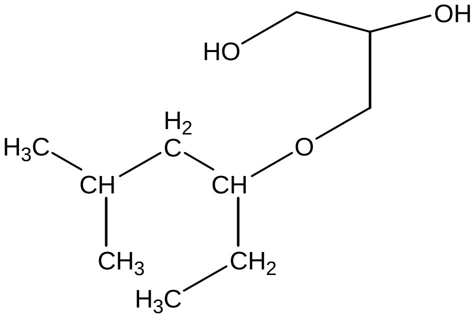
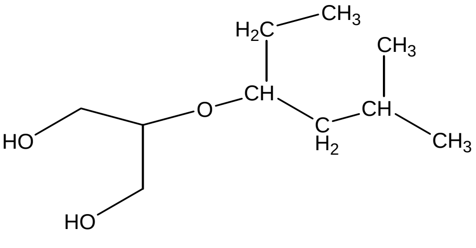
Name	Structure	Sub group
cis-3,4-dimethyl-2-pentene		-CH_3 : 4 >CH-: 1 -CH=C< : 2 CH-C=CH :1 CH3-CH=C :1
2-ethyl-3-methyl-1-butene		-CH_3 : 3 >CH_2 : 1 >CH-: 1 -CH=C<:2 CH2-C=CH2:1
3-(1-methyl-1-isopropyl propoxy)-1,2-propanediol		-CH_3 : 4 >CH_2 : 3 >CH-: 2 >C< : 1 -OH : 2 (CH3)3C: 1 >CH-O-(C) : 1 CH2(OH)CH(OH) : 1
2-(1-methyl-1-isopropyl propoxy)-1,3-propanediol		-CH_3 : 4 >CH_2 : 3 >CH-: 2 >C< : 1 -OH : 2 (CH3)3C: 1 >CH-O-(C) : 1

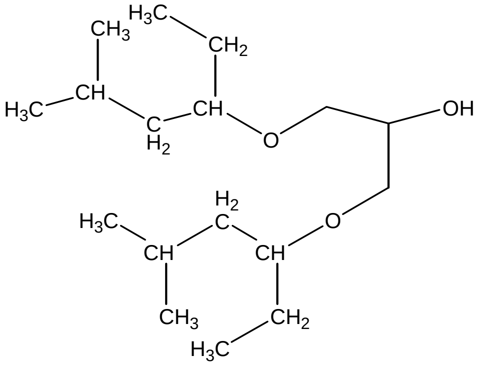
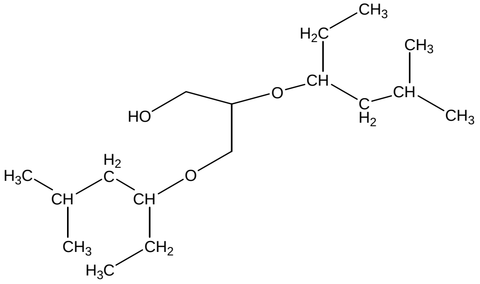
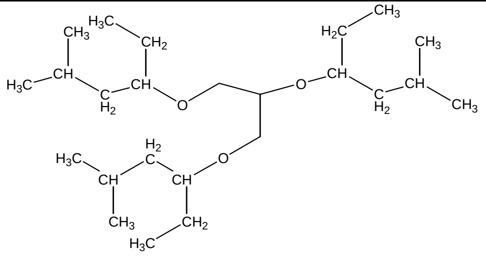
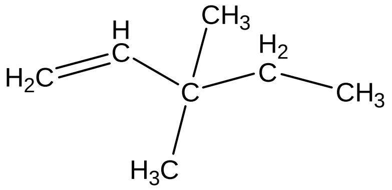
Name	Structure	Sub group
1,3-bis(1-methyl-1-isopropyl propoxy)-2-propanol		-CH_3 : 8 >CH_2 : 4 >CH-: 3 >C< : 2 -OH : 1 (CH3)3C: 2 -CH2-O-(C) : 2
2,3-bis(1-methyl-1-isopropyl propoxy)-1-propanol		-CH_3 : 8 >CH_2 : 4 >CH-: 3 >C< : 2 -OH : 1 (CH3)3C: 2 -CH2-O-(C) : 1 >CH-O-(C) :1
1,2,3-tris(1-methyl-1-isopropyl propoxy)-propane		-CH_3 : 12 >CH_2 : 5 >CH-: 4 >C< : 3 (CH3)3C: 3 -CH2-O-(C) : 2 >CH-O-(C) :1
2, 4-dimethyl-1-pentene		-CH_3 : 3 >CH_2 : 1 >CH-: 2 >C=CH2 : 2 CH2-C=CH2 :1

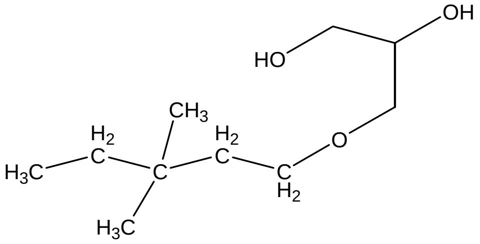
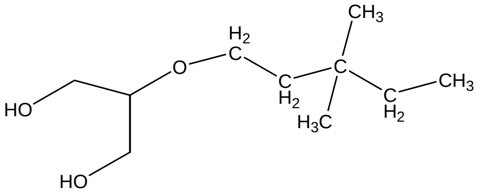
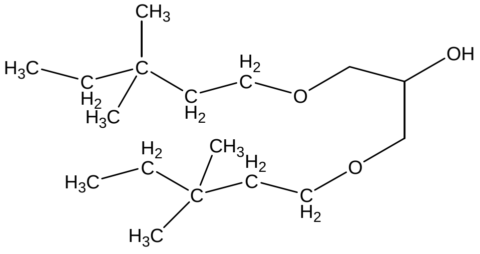
Name	Structure	Sub group
3-(1,1,3-tris methyl butoxy)-1,2-propanediol		-CH$_3$: 4 >CH$_2$: 3 >CH-: 2 >C< : 1 -OH : 2 (CH3)3C: 1 -CH2-O-(C) : 1 >CH-O-(C) : 1 CH2(OH)CH(OH) : 1
2-(1,1,3-tris methyl butoxy)-1,3-propanediol		-CH$_3$: 4 >CH$_2$: 3 >CH-: 2 >C< : 1 -OH : 2 (CH3)3C: 1 >CH-O-(C) : 1 -CH2-O-(C) : 1
1,3-bis(1,1,3-tris methyl butoxy)-2-propanol		-CH$_3$: 8 >CH$_2$: 4 >CH-: 3 >C< : 2 -OH : 1 (CH3)3C: 1 >CH-O-(C) : 1 -CH2-O-(C) : 2

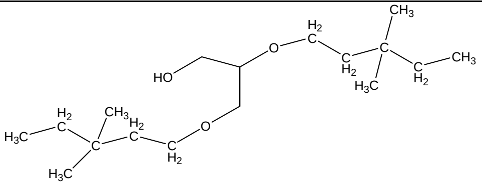
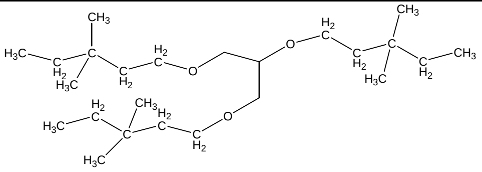
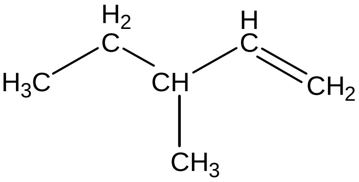
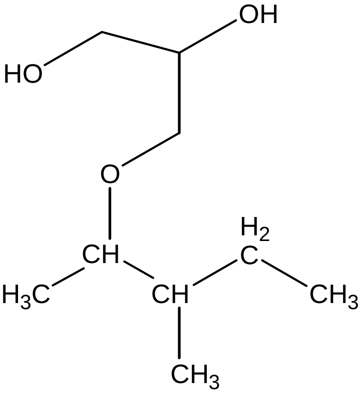
2,3-bis(1,1,3-tris methyl butoxy)-1-propanol		-CH_3 : 8 >CH_2 : 4 >CH-: 3 >C< : 2 -OH : 1 (CH3)3C: 1 >CH-O-(C) : 1 -CH2-O-(C) : 1
1,2,3-tris(1,1,3-tris methyl butoxy)- propane		-CH_3 : 12 >CH_2 : 5 >CH-: 4 >C< : 3 (CH3)3C: 3 >CH-O-(C) : 1 -CH2-O-(C) : 2
3-ethyl-2-pentene		-CH_3 : 3 >CH_2 : 2 -CH=C< : 2 CH2-C=CH :1 CH3=CH=C :1
3-(1,1-diethyl propoxy)-1,2-propanediol		-CH_3 : 3 >CH_2 : 5 >CH-: 1 >C< : 1 -OH : 2 (CH3)3C: 1 -CH2-O-(C) : 1 >CH-O-(C) : 1 CH2(OH)CH(OH) : 1

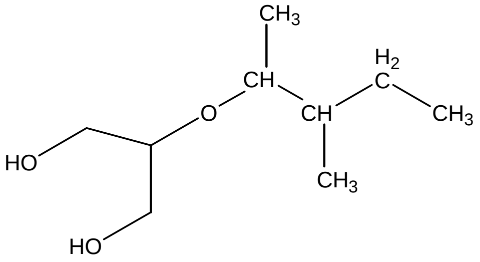
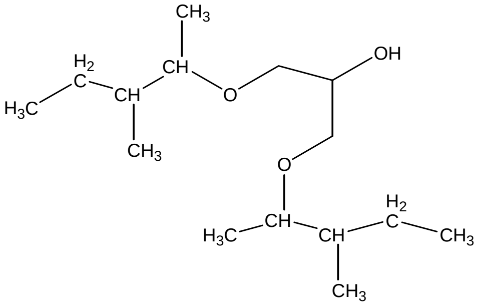
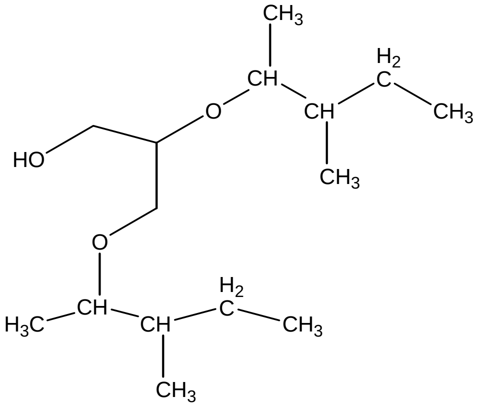
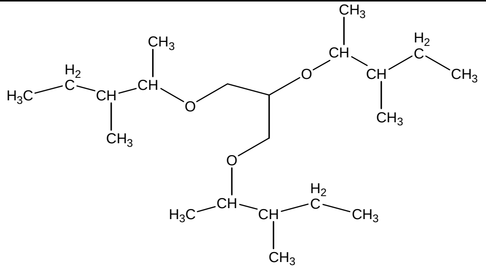
Name	Structure	Sub group
2-(1,1-diethyl propoxy)-1,3-propanediol		-CH_3 : 3 >CH_2 : 5 >CH-: 1 >C< : 1 -OH : 2 (CH3)3C: 1 >CH-O-(C) : 1
1,3-bis(1,1-diethyl propoxy)-2-propanol		-CH_3 : 6 >CH_2 : 8 >CH-: 1 >C< : 2 -OH : 1 (CH3)3C: 2 >CH-O-(C) : 1 -CH2-O-(C) : 2
2,3-bis(1,1-diethyl propoxy)-1-propanol		-CH_3 : 6 >CH_2 : 8 >CH-: 1 >C< : 2 -OH : 1 (CH3)3C: 2 >CH-O-(C) : 1 -CH2-O-(C) : 1

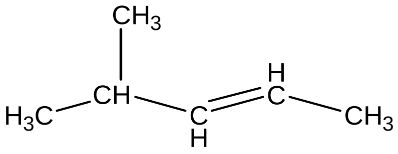
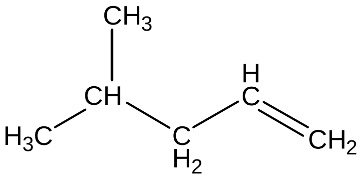
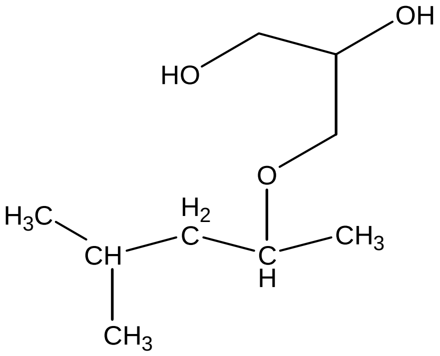
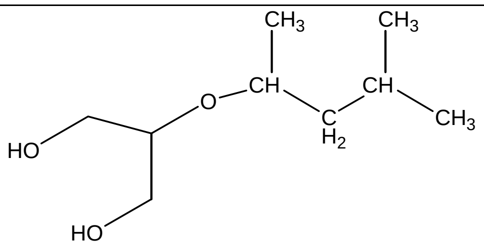
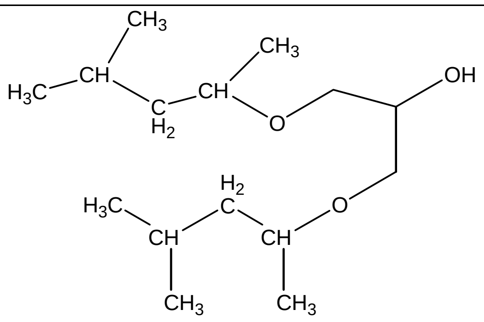
Name	Structure	Sub group
1,2,3-tris(1,1-diethyl propoxy)-propane		$-CH_3$: 9 $>CH_2$: 11 >CH-: 1 >C< : 3 (CH3)3C: 3 >CH-O-(C) : 1 -CH2-O-(C) : 2
Tran-2-methyl-3-hexene		$-CH_3$: 3 $>CH_2$: 1 >CH-: 1 -CH=CH- : 2
3-(1-ethyl-3-methyl butoxy)-1,2-propanediol		$-CH_3$: 3 $>CH_2$: 4 >CH-: 3 -OH : 2 (CH3)3C: 1 -CH2-O-(C) : 1 >CH-O-(C) : 1 CH2(OH)CH(OH) : 1
2-(1-ethyl-3-methyl butoxy)-1,3-propanediol		$-CH_3$: 3 $>CH_2$: 4 >CH-: 3 -OH : 2 (CH3)3C: 1 -CH2-O-(C) : 1 >CH-O-(C) : 1

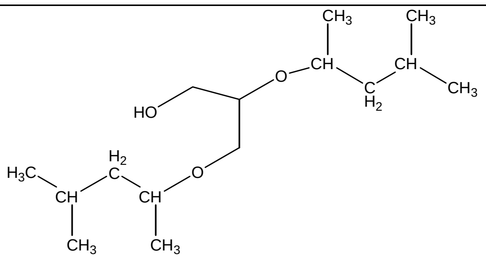
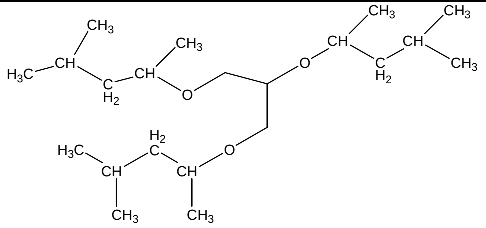
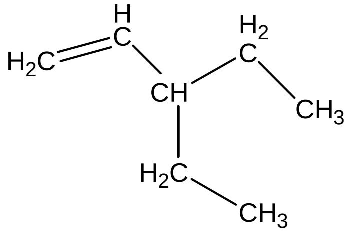
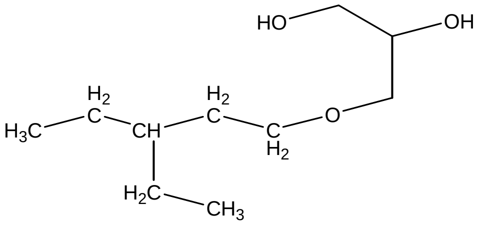
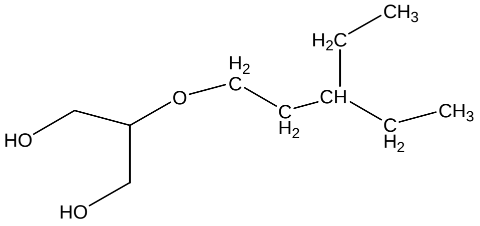
1,3-bis(1-ethyl-3-methyl butoxy)-2-propanol		$-CH_3$: 6 $>CH_2$: 6 >CH-: 5 -OH : 2 (CH3)3C: 2 >CH-O-(C) : 1
2,3-bis(1-ethyl-3-methyl butoxy)-1-propanol		$-CH_3$: 6 $>CH_2$: 6 >CH-: 5 -OH : 2 (CH3)3C: 2 >CH-O-(C) : 1
1,2,3-tris-(1-ethyl-3-methyl butoxy)- propane		$-CH_3$: 9 $>CH_2$: 8 >CH-: 7 (CH3)3C: 3 >CH-O-(C) : 1 -CH2-O-(C) : 2
3,3-dimethyl-1-pentene		$-CH_3$: 3 $>CH_2$: 1 >C<: 1 -CH=CH2 :2

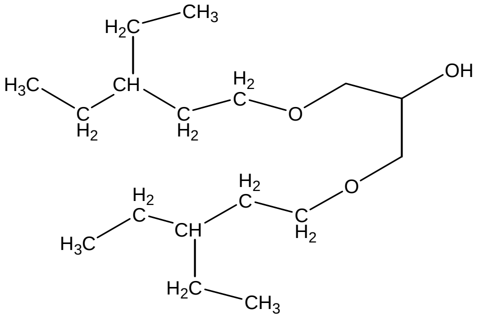
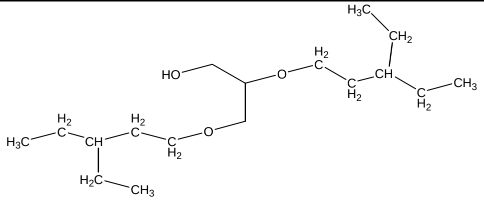
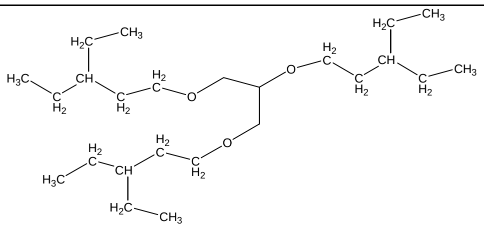
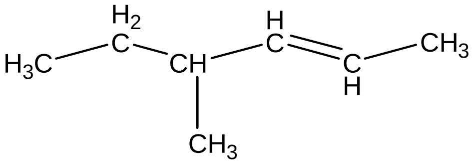
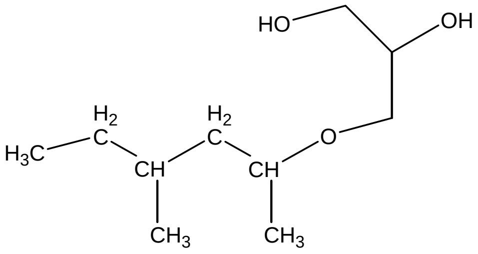
Name	Structure	Sub group
3-(1,1-dimethyl pentoxy)-1,2-propanediol		$-CH_3$: 3 $>CH_2$: 5 >CH-: 1 >C< : 1 -OH : 2 (CH3)3C: 1 -CH2-O-(C) : 1 >CH-O-(C) : 1 CH2(OH)CH(OH) : 1
2-(1,1-dimethyl pentoxy)-1,3-propanediol		$-CH_3$: 3 $>CH_2$: 5 >CH-: 1 >C< : 1 -OH : 2 (CH3)3C: 1 -CH2-O-(C) : 1 >CH-O-(C) : 1
1,3-bis(1,1-dimethyl pentoxy)-2-propanol		$-CH_3$: 6 $>CH_2$: 8 >CH-: 1 >C< : 2 -OH : 1 (CH3)3C: 2 -CH2-O-(C) : 1 >CH-O-(C) : 1

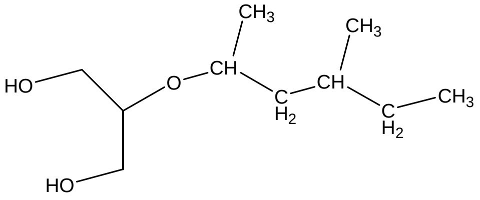
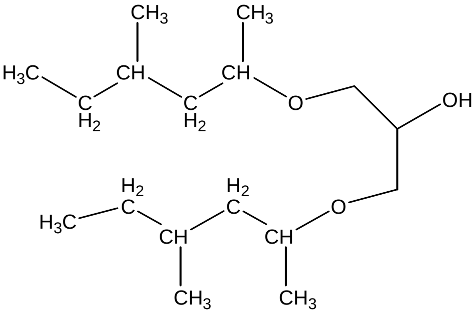
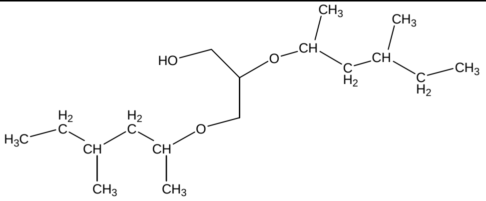
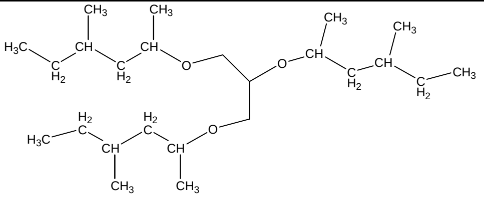
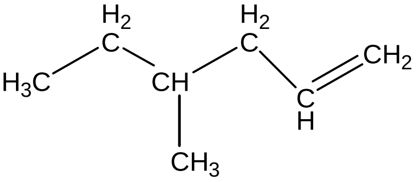
Name	Structure	Sub group
2,3-bis(1,1-dimethyl pentoxy)-1-propanol		$-CH_3$: 6 $>CH_2$: 8 >CH-: 1 >C< : 2 -OH : 1 (CH3)3C: 2 -CH2-O-(C) : 1 >CH-O-(C) : 1
1,2,3-tris-(1,1-dimethyl pentoxy)- propane		$-CH_3$: 9 $>CH_2$: 11 >CH-: 1 >C< : 3 (CH3)3C: 3 -CH2-O-(C) : 1 >CH-O-(C) : 1
3-methyl-1-pentene		CH_3 : 2 $>CH_2$: 1 >CH-: 1 -CH=CH2 : 2
3- (3-ethyl -pentoxy)-1,2-propanediol		$-CH_3$: 3 $>CH_2$: 3 >CH-: 3 -OH : 2 -CH2-O-(C) : 1 >CH-O-(C) : 1 CH2(OH)CH(OH) : 1

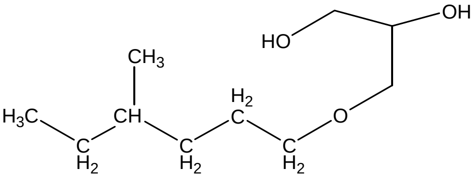
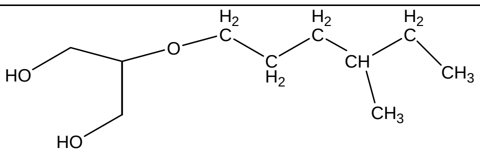
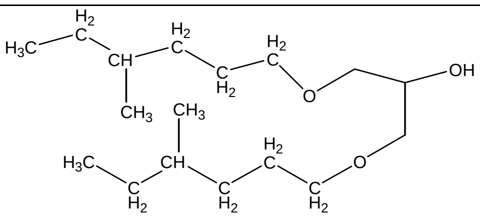
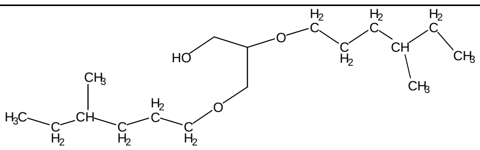
2 -(3-ethyl -pentoxy)-1,3-propanediol		-CH$_3$: 3 >CH$_2$: 3 >CH-: 3 -OH : 2 -CH2-O-(C) : 1 >CH-O-(C) : 1
1,3-bis(3-ethyl-pentoxy)-2-propanol		-CH$_3$: 6 >CH$_2$: 4 >CH-: 5 -OH : 1 -CH2-O-(C) : 2 >CH-O-(C) : 1
2,3-bis(3-ethyl- pentoxy)-1-propanol		-CH$_3$: 6 >CH$_2$: 4 >CH-: 5 -OH : 1 -CH2-O-(C) : 1 >CH-O-(C) : 1
1,2,3-tris-(3-ethyl- pentoxy)-propane		-CH$_3$: 9 >CH$_2$: 5 >CH-: 7 -CH2-O-(C) : 2 >CH-O-(C) : 1

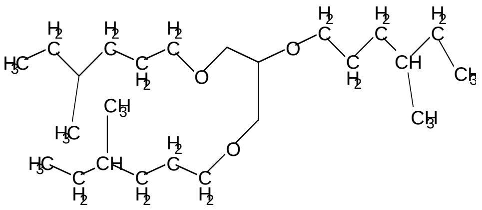
Name	Structure	Sub group
Cis-4-methyl-2-pentene		$-CH_3$: 3 >CH-: 1 -CH=CH- :2
4-methyl-1-pentene		$-CH_3$: 2 $>CH_2$: 2 >CH-: 1 -CH=CH2 : 2
3 -(1,4-dimethyl -butoxy)-1,2-propanediol		$-CH_3$: 3 $>CH_2$: 3 >CH-: 3 -OH : 2 -CH2-O-(C) : 1 >CH-O-(C) : 1 CH2(OH)CH(OH) : 1
2 -(1,4-dimethyl -butoxy)-1,3-propanediol		$-CH_3$: 3 $>CH_2$: 3 >CH-: 3 -OH : 2 -CH2-O-(C) : 1 >CH-O-(C) : 1
1,3-bis(1,4-dimethyl- butoxy)-2-propanol		$-CH_3$: 6 $>CH_2$: 4 >CH-: 5 -OH : 1 -CH2-O-(C) : 2

Name	Structure	Sub group
2,3-bis(1,4-dimethyl- butoxy)-1-propanol		-CH$_3$: 6 >CH$_2$: 4 >CH-: 5 -OH : 1 -CH2-O-(C) : 1 >CH-O-(C) : 1
1,2,3-tris-(1,4-dimethyl-butoxy)- propane		-CH$_3$: 9 >CH$_2$: 5 >CH-: 7 -CH2-O-(C) : 2 >CH-O-(C) : 1
3-ethyl-1-pentene		-CH$_3$: 2 >CH$_2$: 2 >CH-: 1 -CH=CH2 : 2
3-(1-methyl-2-ethyl-butoxy)-1,2-propanediol		-CH$_3$: 2 >CH$_2$: 6 >CH-: 2 -OH : 2 -CH2-O-(C) : 1 >CH-O-(C) : 1 CH2(OH)CH(OH) : 1
2-(1-methyl-2-ethyl-butoxy)-1,3-propanediol		-CH$_3$: 2 >CH$_2$: 6 >CH-: 2 -OH : 2 -CH2-O-(C) : 1 >CH-O-(C) : 1

Name	Structure	Sub group
1,3-bis(1-methyl-2-ethyl-butoxy)-2-propanol		$-CH_3$: 4 $>CH_2$: 8 >CH-: 3 -OH : 1 -CH2-O-(C) : 2 >CH-O-(C) : 1
2,3-bis(1-methyl-2-ethyl-butoxy)-1-propanol		$-CH_3$: 4 $>CH_2$: 8 >CH-: 3 -OH : 1 -CH2-O-(C) : 1 >CH-O-(C) : 1
1,2,3-tris-(1-methyl-2-ethyl-butoxy)- propane		$-CH_3$: 6 $>CH_2$: 10 >CH-: 4 -CH2-O-(C) : 2 >CH-O-(C) : 1
Cis-5-methyl-2-hexene		$-CH_3$: 3 $>CH_2$: 1 >CH-: 1 -CH=CH- : 2
3-(1,3-dimethyl-pentoxy)-1,2-propanediol		$-CH_3$: 3 $>CH_2$: 4 >CH-: 3 -OH : 2 -CH2-O-(C) : 1 >CH-O-(C) : 1 CH2(OH)CH(OH) : 1

Name	Structure	Sub group
2-(1,3-dimethyl-pentoxy)-1,3-propanediol		-CH_3 : 3 >CH_2 : 4 >CH-: 3 -OH : 2 -CH2-O-(C) : 1 >CH-O-(C) : 1
1,3-bis(1,3-dimethyl-pentoxy)-2-propanol		-CH_3 : 4 >CH_2 : 6 >CH-: 5 -OH : 1 -CH2-O-(C) : 2 >CH-O-(C) : 1
2,3-bis(1,3-dimethyl-pentoxy)-1-propanol		-CH_3 : 4 >CH_2 : 6 >CH-: 5 -OH : 1 -CH2-O-(C) : 1 >CH-O-(C) : 1
1,2,3-tris-(1,3-dimethyl-pentoxy)- propane		-CH_3 : 9 >CH_2 : 8 >CH-: 7 -CH2-O-(C) : 2 >CH-O-(C) : 1
4-methyl-1-hexene		-CH_3 : 2 >CH_2 : 2 >CH-: 1 -CH=CH2 : 2

Name	Structure	Sub group
3-(4-methyl-hexoxy)-1,2-propanediol		-CH_3 : 2 >CH_2 : 6 >CH-: 2 -OH : 2 -CH2-O-(C) : 1 >CH-O-(C) : 1 CH2(OH)CH(OH) : 1
2-(4-methyl-hexoxy)-1,3-propanediol		-CH_3 : 2 >CH_2 : 6 >CH-: 2 -OH : 2 >CH-O-(C) : 1
1,3-bis(4-methyl-hexoxy)-2-propanol		-CH_3 : 4 >CH_2 : 10 >CH-: 3 -OH : 1 -CH2-O-(C) : 2
2,3-bis(4-methyl-hexoxy)-1-propanol		-CH_3 : 4 >CH_2 : 10 >CH-: 3 -OH : 1 -CH2-O-(C) : 1 >CH-O-(C) : 1

1,2,3-tris-(4-methyl-hexoxy)-propane		-CH_3 : 6 >CH_2 : 14 >CH-: 4 -CH2-O-(C) : 2 >CH-O-(C) : 1

Note: Gani's subgroup (Aspen subgroup ID) will be listed below;

First order; -CH3 (1015), >CH2 (1010), >CH- (1005), >C< (1000), -CH=CH2 (1070), -CH=CH- (1065), >C=CH2 (1060), >C=C< (1050), -OH alcohol (1200), -CH2-O-C non-ring (1610).

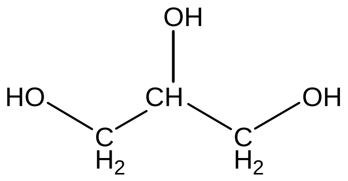
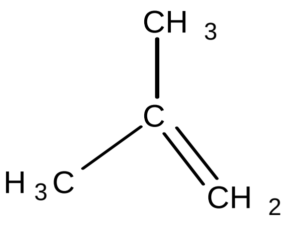
Second order; (CH3)2CH- (5000), -C(CH3)2C(CH3)2- (5020), CH3-C=CH2 (5175), CH2-C=CH2 (5205), CH-C=CH2 (5235), 5-member ring correction (5035), 6-member ring correction (5040),

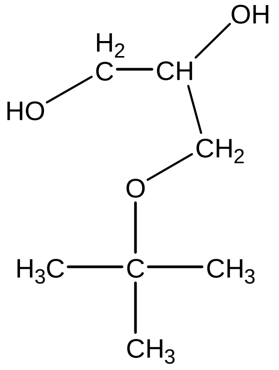
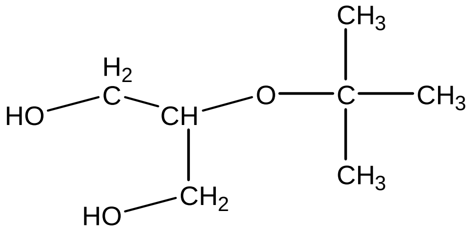
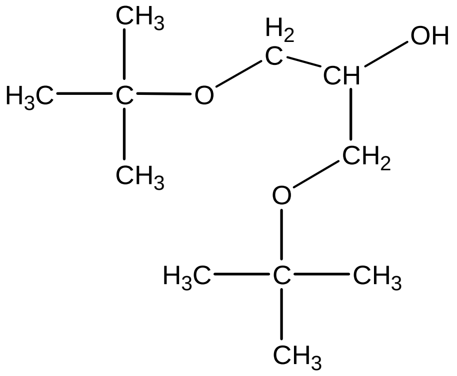
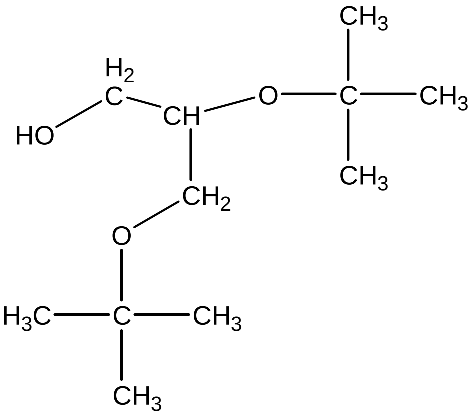
APPENDIX C

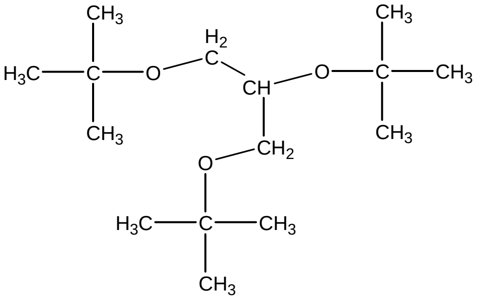
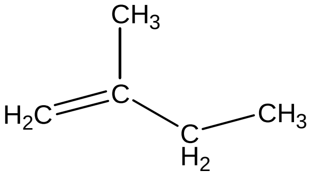
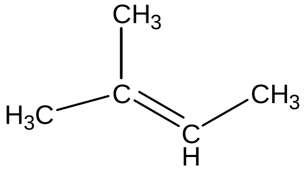
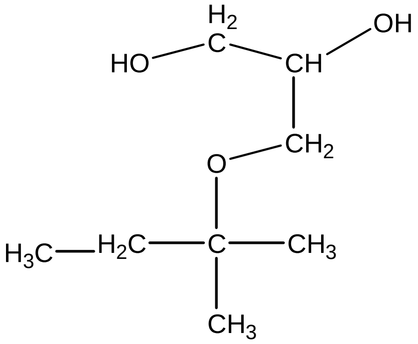
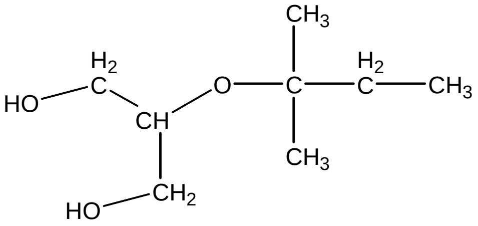
BENSON’S GROUP CONTRIBUTION METHOD

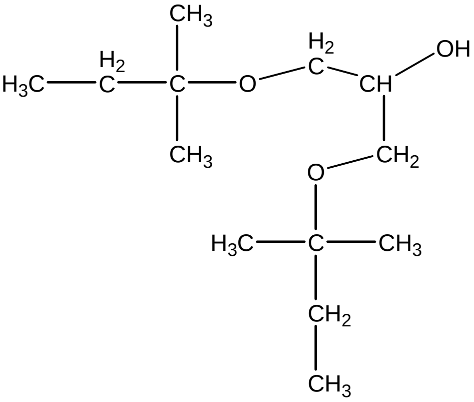
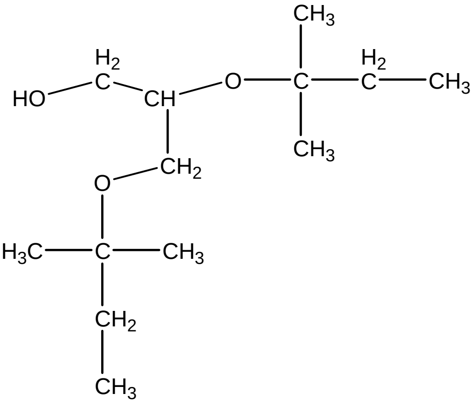
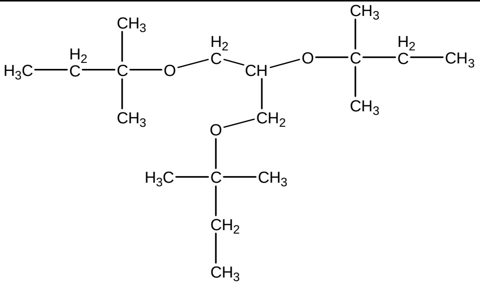
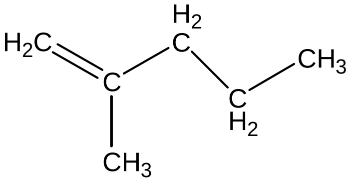
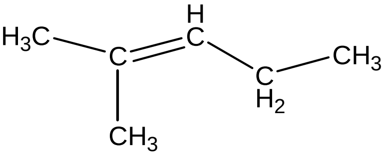
The functional groups of components in olefins are listed below with the number of subgroup in each component. Benson’s group contribution method is used to estimate the property of olefin components. This method will be used to estimate thermodynamic properties, Gibbs of formation.

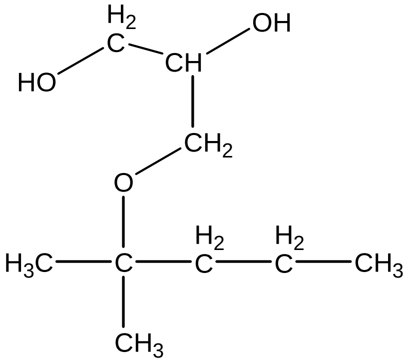
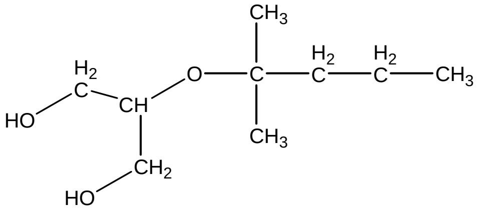
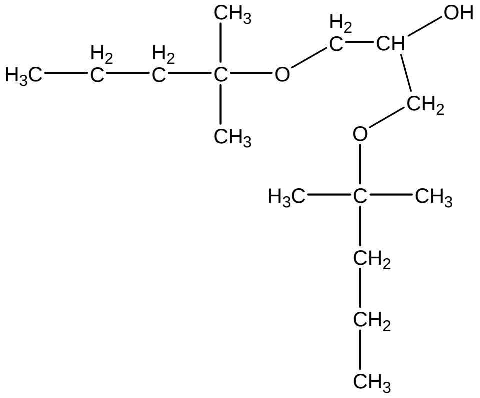
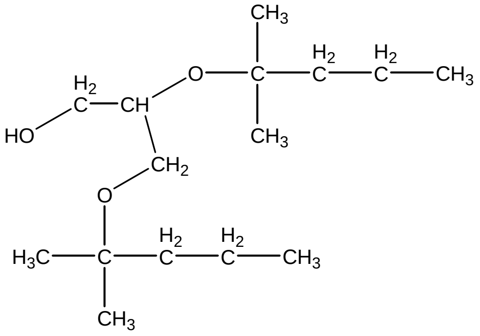
Table A. Sub group of components

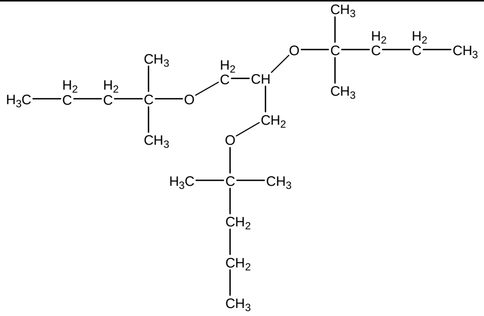
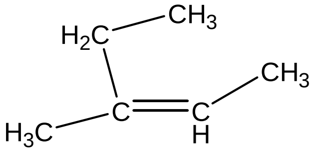
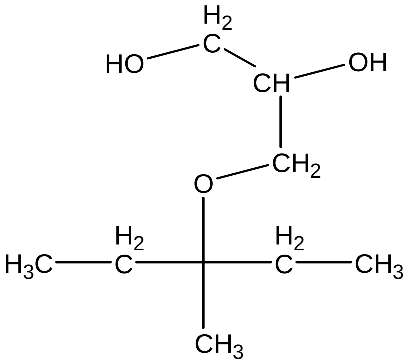
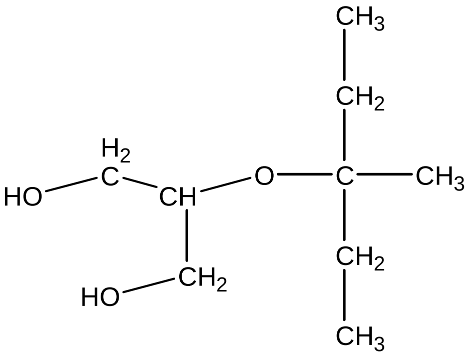
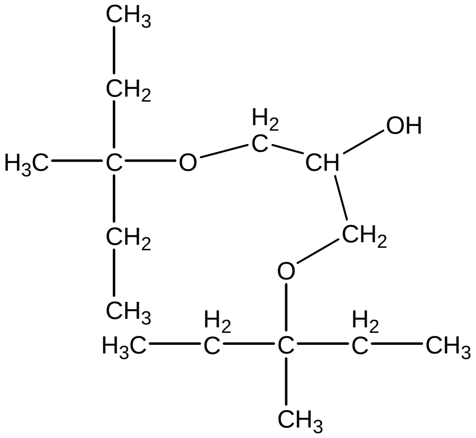
Name	Structure	Sub group
Glycerol		CH_2-(C,O):2 CH-(2C,O) : 1 OH-(C) : 3
Isobutene		CH_3-(C) : 2 =CH_2: 1 =C-(2C) : 1

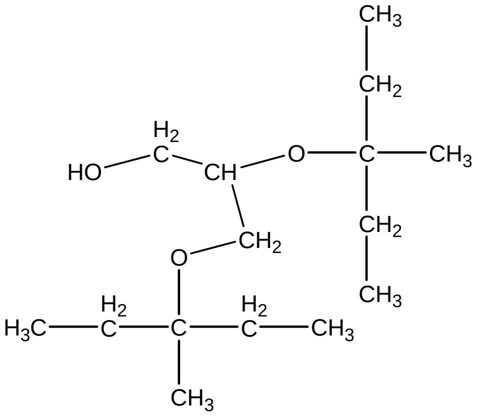
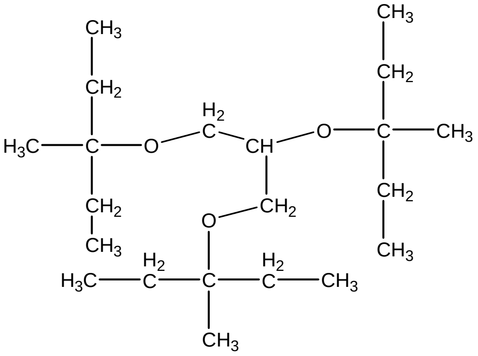
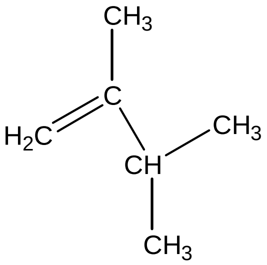
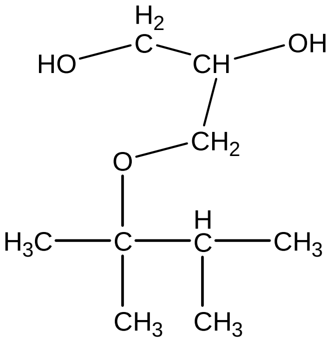
Name	Structure	Sub group
3-tert-butoxy -1,2-propanediol		CH_3-(C) : 3 CH_2-(C,O):2 CH-(2C,O) : 1 O-(2C) : 1 OH-(C) : 2 C-(3C,O) : 1
2-tert-butoxy -1,3-propanediol		CH_3-(C) : 3 CH_2-(C,O):2 CH-(2C,O) : 1 O-(2C) : 1 C-(3C,O) : 1 OH-(C) : 2
1,3-di-tert-butoxy-2-propanol		CH_3-(C) : 6 CH_2-(C,O):2 CH-(2C,O) : 1 O-(2C) : 2 C-(3C,O) : 2 OH-(C) : 1
2,3-di-tert-butoxy-1-propanol		CH_3-(C) : 6 CH_2-(C,O):2 CH-(2C,O) : 1 O-(2C) : 2 C-(3C,O) : 2 OH-(C) : 1

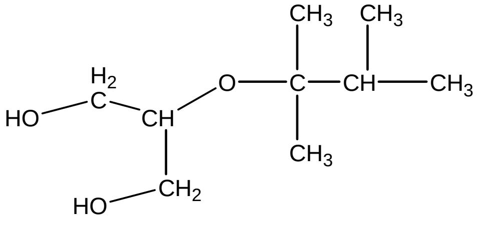
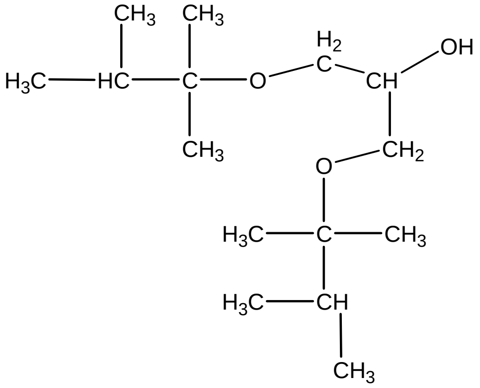
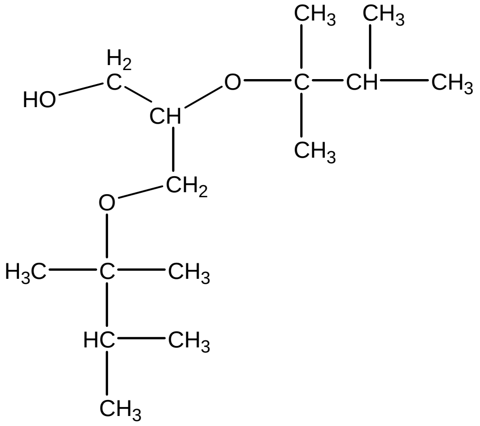
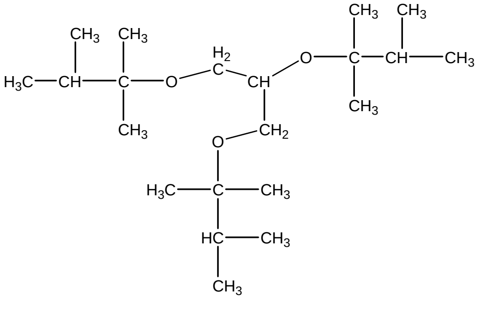
Name	Structure	Sub group
1,2,3- tri-tert-butoxy-propane		CH_3-(C) : 9 CH_2-(C,O):2 CH-(2C,O) : 1 O-(2C) : 3 C-(3C,O) : 3
2-methyl-1-butene		CH3-(C): 1 =CH2 :1 =C-(2C) : 1 CH3-(=C) :1 CH2-(C,=C) :1
2-methyl-2-butene		=C-(2C) : 1 =CH-(=C) : 2 CH3-(=C) :1 CH2-(C,=C) : 1
3(1,1-dimethyl-propoxy)-1,2-propanediol		CH_3-(C) : 3 CH2-(2C) : 1 O-(2C) : 1 OH-(C) : 2 C-(3C,O) : 1 CH-(2C,O) : 1 CH_2-(C,O):2
2(1,1-dimethyl-propoxy)-1,3-propanediol		CH_3-(C) : 3 CH2-(2C) : 1 O-(2C) : 1 OH-(C) : 2 C-(3C,O) : 1 CH-(2C,O) : 1 CH_2-(C,O):2

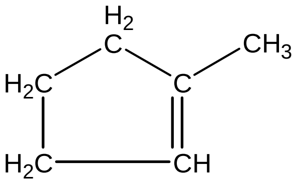
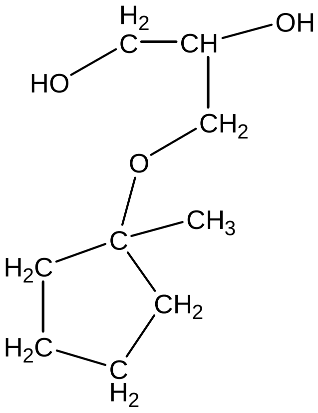
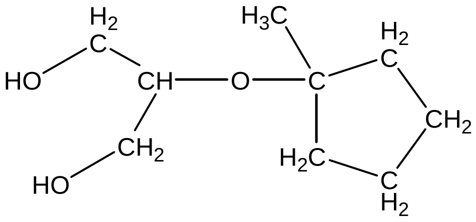
1,3-bis-(1,1-dimethyl propoxy) -2-propanol		CH_3-(C) : 6 CH2-(2C) : 2 O-(2C) : 2 OH-(C) : 1 C-(3C,O) : 2 CH-(2C,O) : 1 CH_2-(C,O):2
2,3-bis-(1,1-dimethyl propoxy) -1-propanol		CH_3-(C) : 6 CH2-(2C) : 2 O-(2C) : 2 OH-(C) : 1 C-(3C,O) : 2 CH-(2C,O) : 1 CH_2-(C,O):2
1,2,3-tris-(1,1-dimethyl propoxy)-propane		CH_3-(C) : 9 CH2-(2C) : 3 O-(2C) : 3 C-(3C,O) : 3 CH-(2C,O) : 1 CH_2-(C,O):2
2-methyl-1-pentene		CH_3-(C) : 1 CH2-(2C) : 1 =CH2 : 1 =C-(2C) : 1 CH3-(=C) : 1 CH2-(C,=C): 1
2-methyl-2-pentene		CH_3-(C) : 1 =C-(2C) : 1 =C-(2C) : 2 CH3-(=C) : 2

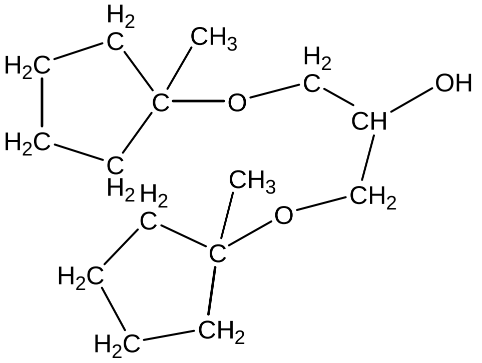
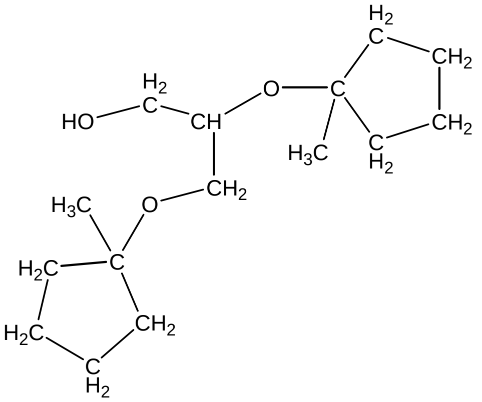
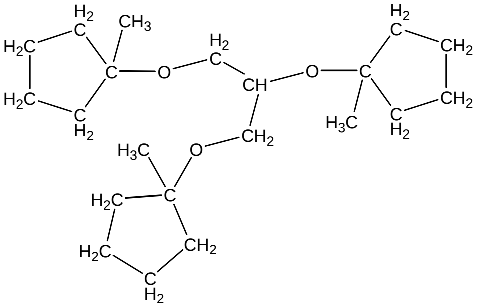
3-(1,1-dimethyl butoxy)-1,2-propanediol		CH_3-(C) : 3 CH2-(2C) : 2 O-(2C) : 1 OH-(C) : 2 C-(3C,O) : 1 CH-(2C,O) : 1 CH_2-(C,O):2
2-(1,1-dimethyl butoxy)-1,3-propanediol		CH_3-(C) : 3 CH2-(2C) : 2 O-(2C) : 1 OH-(C) : 2 C-(3C,O) : 1 CH-(2C,O) : 1 CH_2-(C,O):2
1,3-bis (1,1-dimethyl butoxy)-2-propanol		CH_3-(C) : 6 CH2-(2C) : 4 O-(2C) : 2 OH-(C) : 1 C-(3C,O) : 2 CH-(2C,O) : 1 CH_2-(C,O):2
2,3-bis (1,1-dimethyl butoxy)-1-propanol		CH_3-(C) : 6 CH2-(2C) : 4 O-(2C) : 2 OH-(C) : 1 C-(3C,O) : 2 CH-(2C,O) : 1 CH_2-(C,O):2

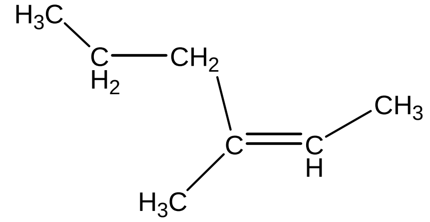
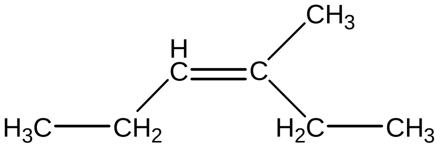
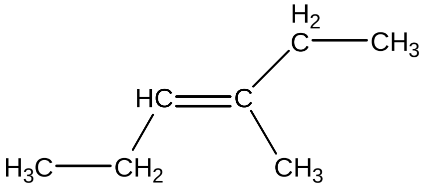
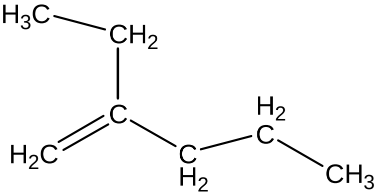
1,2,3-tris(1,1-dimethyl butoxy)-propane		CH_3-(C) : 9 CH2-(2C) : 6 O-(2C) : 3 C-(3C,O) : 3 CH-(2C,O) : 1 CH_2-(C,O):2
cis-3-methyl-2-pentene		CH_3-(C) : 1 =C-(C) : 2 =CH-(=C) : 1 CH3-(=C) : 1 CH2-(C,=C): 1
3-(1-methyl-2-ethyl-propoxy)-1,2-propanediol		CH_3-(C) : 3 CH2-(2C) : 2 O-(2C) : 1 OH-(C) : 2 C-(3C,O) : 1 CH-(2C,O) : 1 CH_2-(C,O):2
2-(1-methyl-2-ethyl-propoxy)-1,3-propanediol		CH_3-(C) : 3 CH2-(2C) : 2 O-(2C) : 1 OH-(C) : 2 C-(3C,O) : 1 CH-(2C,O) : 1 CH_2-(C,O):2
1,3-bis (1,1-methyl-2-ethyl-propoxy)-2- propanol		CH_3-(C) : 6 CH2-(2C) : 4 O-(2C) : 2 OH-(C) : 1 C-(3C,O) : 2 CH-(2C,O) : 1 CH_2-(C,O):2

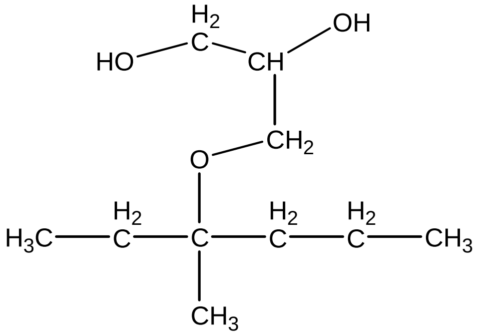
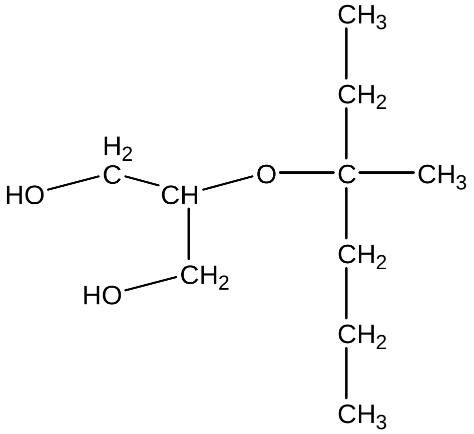
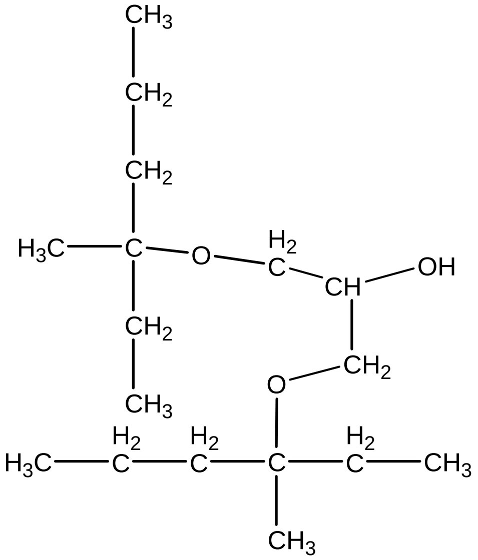
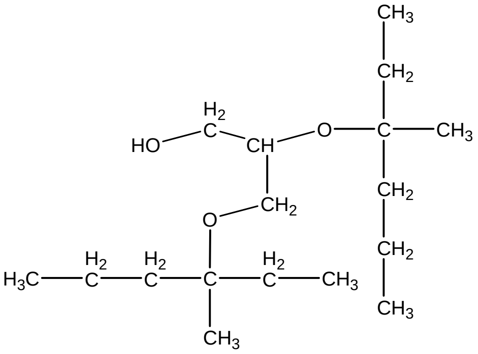
2,3-bis (1,1-methyl-2-ethyl -propoxy)-1- propanol		CH_3-(C) : 6 CH2-(2C) : 4 O-(2C) : 2 OH-(C) : 1 C-(3C,O) : 2 CH-(2C,O) : 1 CH_2-(C,O):2
1,2,3-tris (1-methyl-2-ethyl-propoxy)- propane		CH_3-(C) : 9 CH2-(2C) : 6 O-(2C) : 3 C-(3C,O) : 3 CH-(2C,O) : 1 CH_2-(C,O):2
2,3-dimethyl-1-butene		CH_3-(C) : 2 =CH2 : 1 =C-(2C) : 1 =C(C,=C) : 1 CH-(2C,=C): 1
3-(1,1,2-trimethyl-propoxy)-1,2-propanediol		CH_3-(C) : 4 CH-(3C) : 1 O-(2C) : 1 OH-(C) : 2 C-(3C,O) : 1 CH-(2C,O) : 1 CH_2-(C,O):2

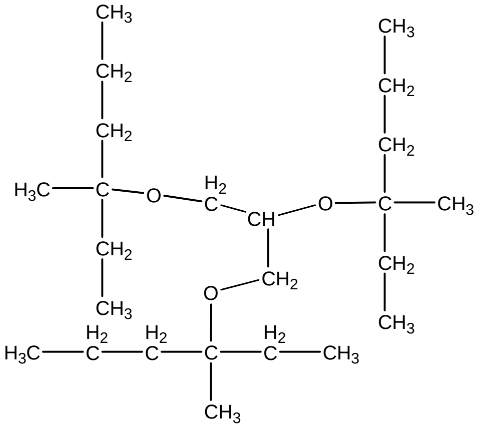
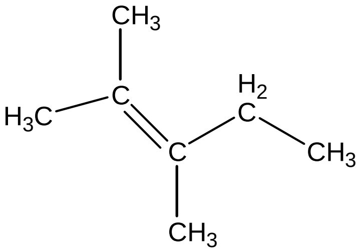
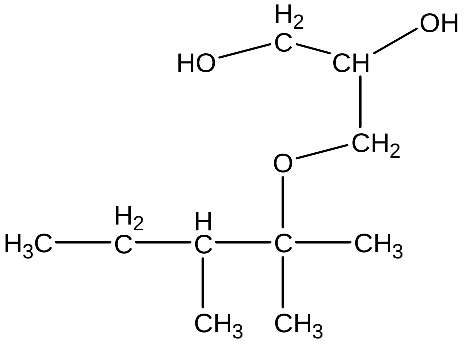
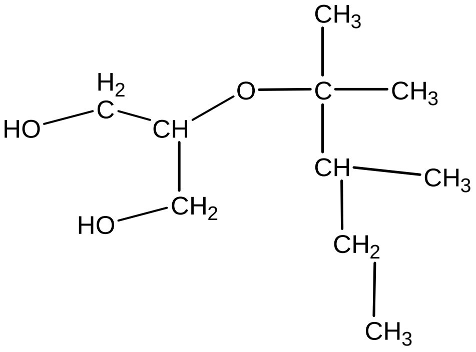
2-(1,1,2-trimethyl-propoxy)-1,3-propanediol		CH_3-(C) : 4 CH-(3C) : 1 O-(2C) : 1 OH-(C) : 2 C-(3C,O) : 1 CH-(2C,O) : 1 CH_2-(C,O):2
1,3-bis(1,1,2-trimethyl-propoxy)-2-propanol		CH_3-(C) : 8 CH-(3C) : 2 O-(2C) : 2 OH-(C) : 1 C-(3C,O) : 2 CH-(2C,O) : 1 CH_2-(C,O):2
2,3-bis(1,1,2-trimethyl-propoxy)-1-propanol		CH_3-(C) : 8 CH-(3C) : 2 O-(2C) : 2 OH-(C) : 1 C-(3C,O) : 2 CH-(2C,O) : 1 CH_2-(C,O):2
1,2,3-tris(1,1,2-trimethyl-propoxy)-propane		CH_3-(C) : 12 CH-(3C) : 3 O-(2C) : 3 C-(3C,O) : 3 CH-(2C,O) : 1 CH_2-(C,O):2

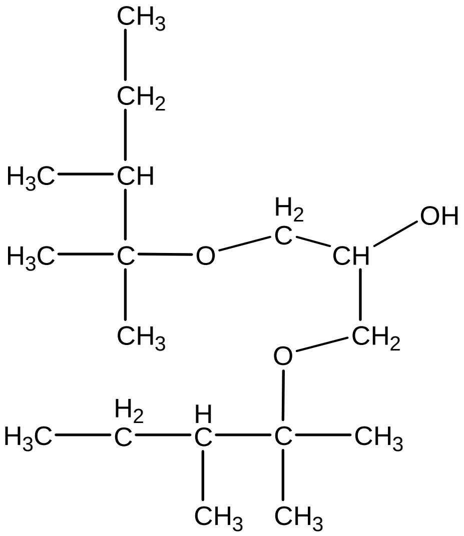
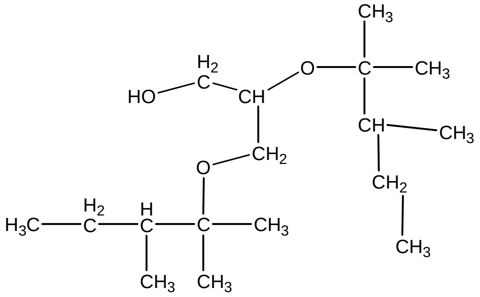
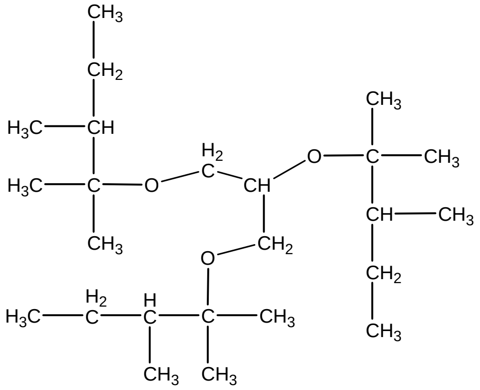
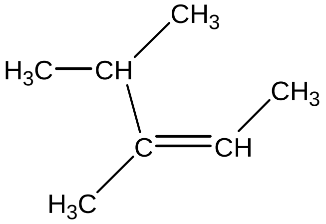
1-methylcyclopentene		CH2-(2C) : 1 =C-(2C) : 1 =CH-(=C) : 1 CH2-(C,=C) : 2 =C- (C,=C) : 1 Clyclopentene:1
3-(1,1,2-trimethyl-propoxy)-1,2-propanediol		CH_3-(C) : 1 CH2-(2C) : 4 O-(2C) : 1 OH-(C) : 2 C-(3C,O) : 1 CH-(2C,O) : 1 CH_2-(C,O):2
2-(1,1,2-trimethyl-propoxy)-1,3-propanediol		CH_3-(C) : 1 CH2-(2C) : 4 O-(2C) : 1 OH-(C) : 2 C-(3C,O) : 1 CH-(2C,O) : 1 CH_2-(C,O):2

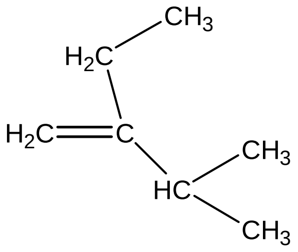
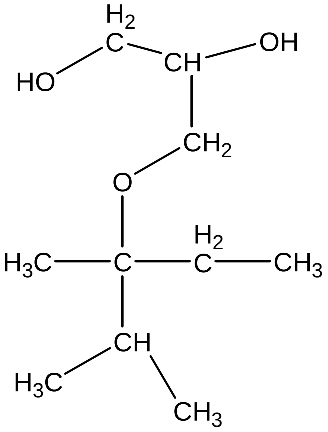
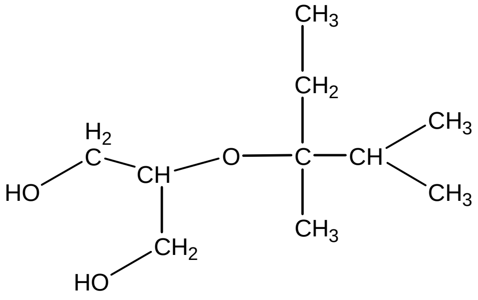
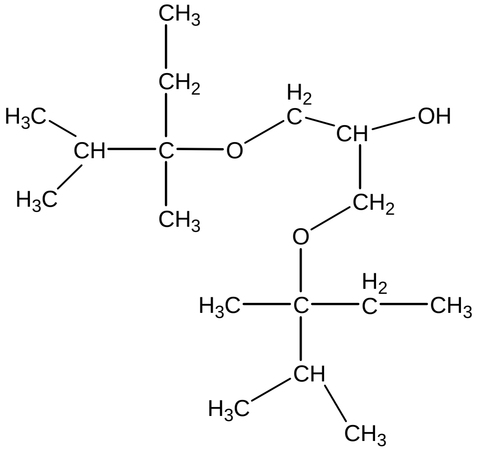
Name	Structure	Sub group
1,3-bis-(1-methyl cyclopentyloxy)-2-propanol		CH_3-(C) : 2 CH2-(2C) : 8 O-(2C) : 2 OH-(C) : 1 C-(3C,O) : 2 CH-(2C,O) : 1 CH_2-(C,O):2
2,3-bis-(1-methyl cyclopentyloxy)-1-propanol		CH_3-(C) : 2 CH2-(2C) : 8 O-(2C) : 2 OH-(C) : 1 C-(3C,O) : 2 CH-(2C,O) : 1 CH_2-(C,O):2
1,2,3-tris(1-methyl cylopentyloxy)-propane		CH_3-(C) : 3 CH2-(2C) : 12 O-(2C) : 3 C-(3C,O) : 3 CH-(2C,O) : 1 CH_2-(C,O):2

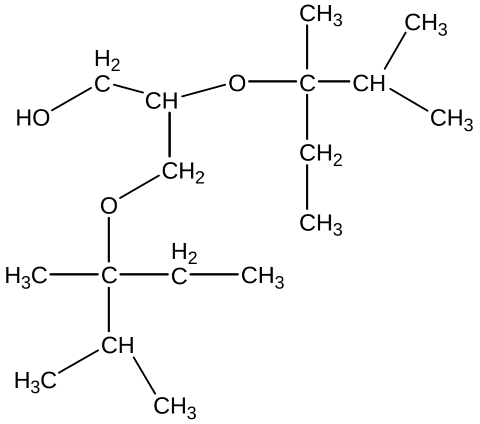
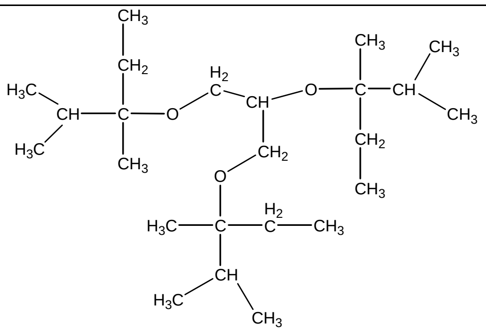
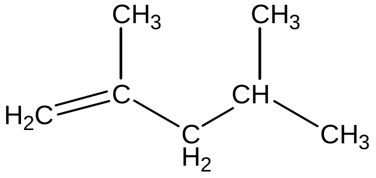
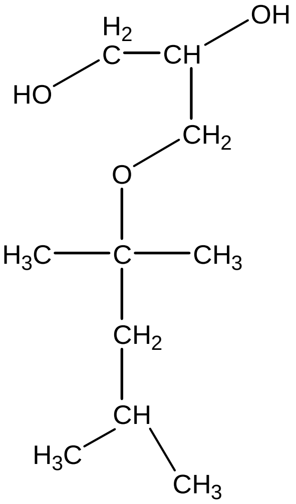
Name	Structure	Sub group
cis-3-methyl-2-hexene		CH3-(C) : 1 CH2-(2C) :1 =C –(C) :1 =C-(2C):1 CH3-(=C) : 2 CH2-(C,=C):1
cis-3-methyl-3-hexene		CH3-(C) : 2 CH2-(2C) :1 =C –(C) :1 =C-(2C):1 CH3-(=C) : 1 CH2-(C,=C):2
trans-3-methyl-3-hexene		CH3-(C) : 2 CH2-(2C) :1 =C –(C) :1 =C-(2C):1 CH3-(=C) : 1 CH2-(C,=C):2
2-ethyl-1-pentene		CH3-(C) : 2 CH2-(2C) : 1 =CH2 : 1 =C-(2C):1 CH2-(C,=C):2

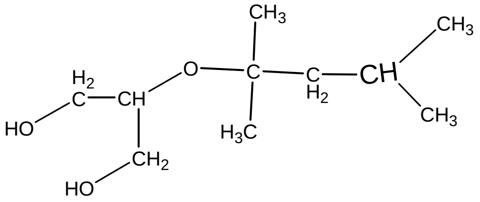
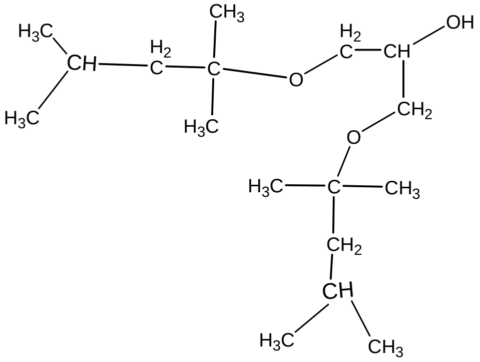
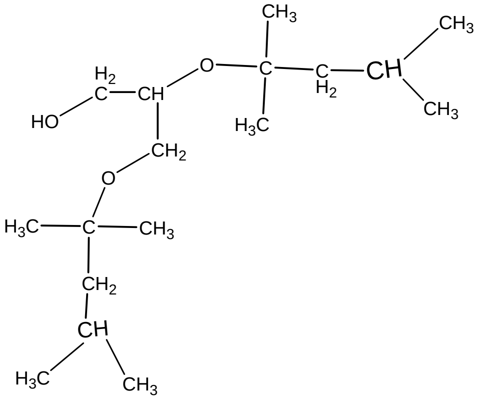
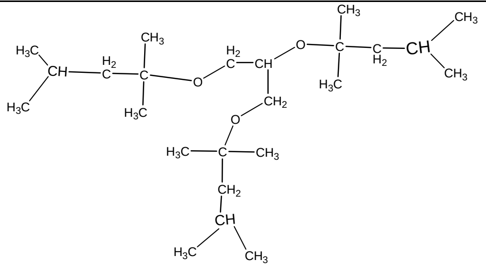
3-(1-methyl-1-ethyl-butoxy)-1,2-propanediol		CH_3-(C) : 3 CH2-(2C) : 3 O-(2C) : 1 OH-(C) : 2 C-(3C,O) : 1 CH-(2C,O) : 1 CH_2-(C,O):2
2-(1-methyl-1-ethyl-butoxy)-1,3-propanediol		CH_3-(C) : 3 CH2-(2C) : 3 O-(2C) : 1 OH-(C) : 2 C-(3C,O) : 1 CH-(2C,O) : 1 CH_2-(C,O):2
1,3-bis(1-methyl-1-ethyl-butoxy)-2-propanol		CH_3-(C) : 6 CH2-(2C) : 6 O-(2C) : 2 OH-(C) : 1 C-(3C,O) : 2 CH-(2C,O) : 1 CH_2-(C,O):2
2,3-bis(1-methyl-1-ethyl-butoxy)-1-propanol		CH_3-(C) : 6 CH2-(2C) : 6 O-(2C) : 2 OH-(C) : 1 C-(3C,O) : 2 CH-(2C,O) : 1 CH_2-(C,O):2

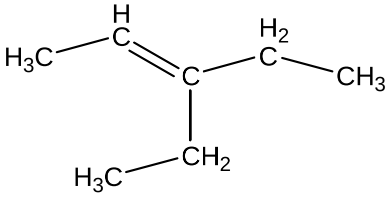
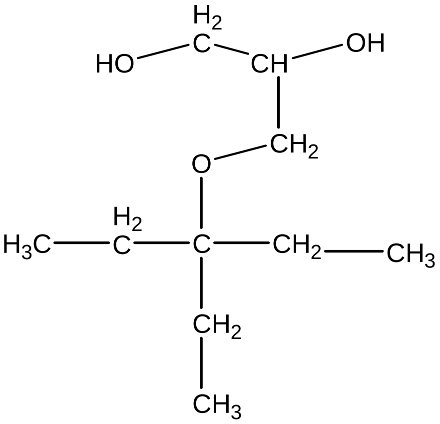
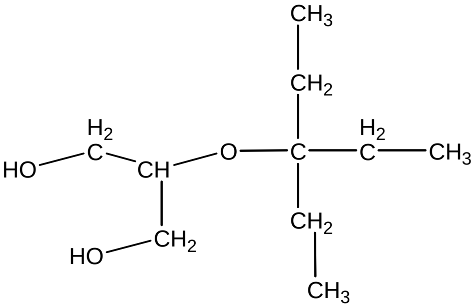
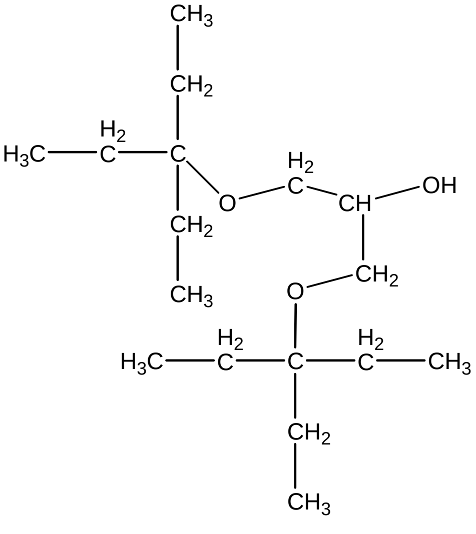
1,2,3-tris(1-methyl-1-ethyl-butoxy)- propane		CH_3-(C) : 9 CH2-(2C) : 9 O-(2C) : 3 C-(3C,O) : 3 CH-(2C,O) : 1 CH_2-(C,O):2
2, 3-dimethyl-2-pentene		CH3-(C) : 1 =C-(2C) : 2 CH3-(=C) : 3 CH2-(C,=C): 1
3-(1,1,2-trimethyl-butoxy)-1,2-propanediol		CH_3-(C) : 4 CH2-(2C) : 1 CH-(3C) : 1 O-(2C) : 1 OH-(C) : 2 C-(3C,O) : 1 CH-(2C,O) : 1 CH_2-(C,O):2
2-(1,1,2-trimethyl-butoxy)-1,3-propanediol		CH_3-(C) : 4 CH2-(2C) : 1 CH-(3C) : 1 O-(2C) : 1 OH-(C) : 2 C-(3C,O) : 1 CH-(2C,O) : 1 CH_2-(C,O):2

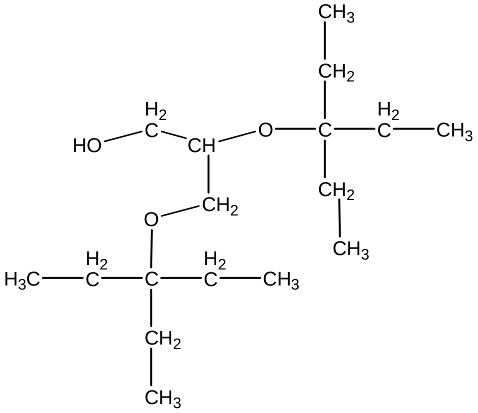
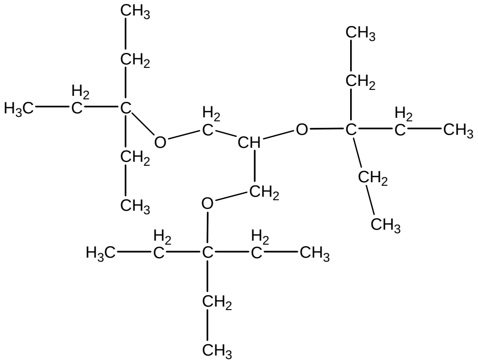
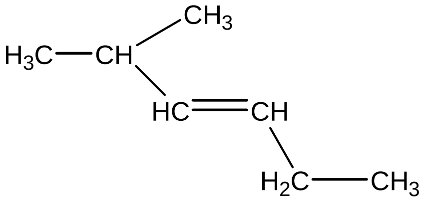
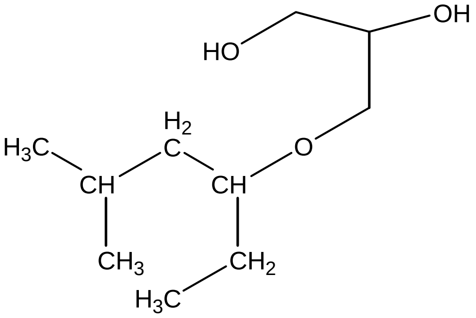
1,3-bis(1,1,2-trimethyl-butoxy)-2-propanol		CH$_3$-(C) : 8 CH2-(2C) : 2 CH-(3C) : 2 O-(2C) : 2 OH-(C) : 1 C-(3C,O) : 2 CH-(2C,O) : 1 CH$_2$-(C,O):2
2,3-bis(1,1,2-trimethyl-butoxy)-1-propanol		CH$_3$-(C) : 8 CH2-(2C) : 2 CH-(3C) : 2 O-(2C) : 2 OH-(C) : 1 C-(3C,O) : 2 CH-(2C,O) : 1 CH$_2$-(C,O):2
1,2,3-tris(1,1,2-trimethyl-butoxy)- propane		CH$_3$-(C) : 12 CH2-(2C) : 3 CH-(3C) : 3 O-(2C) : 3 C-(3C,O) : 3 CH-(2C,O) : 1 CH$_2$-(C,O):2
cis-3,4-dimethyl-2-pentene		CH3-(C): 2 =C-(C) :1 =C-(2C) : 1 CH3-(=C) : 2 CH-(2C,=C): 1

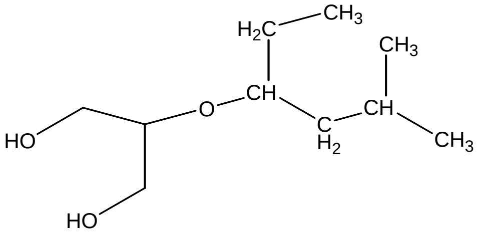
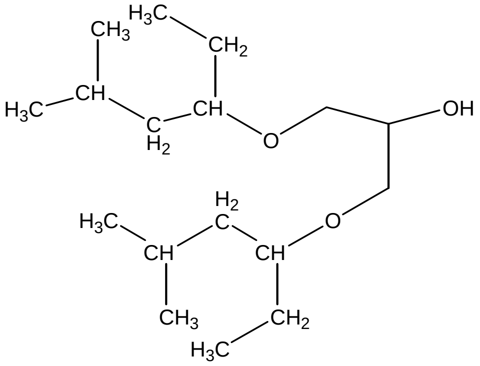
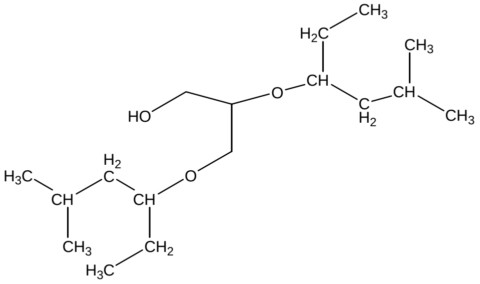
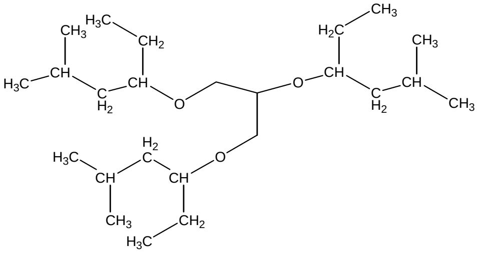
2-ethyl-3-methyl-1-butene		CH3-(C) : 3 =CH2 : 1 =C –(2C) : 1 CH2-(C,=C):1 CH-(2C,=C):1
3-(1-methyl-1-isopropyl propoxy)-1,2-propanediol		CH_3-(C) : 4 CH2-(2C) : 1 CH-(3C) : 1 O-(2C) : 1 OH-(C) : 2 C-(3C,O) : 1 CH-(2C,O) : 1 CH_2-(C,O):2
2-(1-methyl-1-isopropyl propoxy)-1,3-propanediol		CH_3-(C) : 4 CH2-(2C) : 1 CH-(3C) : 1 O-(2C) : 1 OH-(C) : 2 C-(3C,O) : 1 CH-(2C,O) : 1 CH_2-(C,O):2
1,3-bis(1-methyl-1-isopropyl propoxy)-2-propanol		CH_3-(C) : 8 CH2-(2C) : 2 CH-(3C) : 2 O-(2C) : 2 OH-(C) : 1 C-(3C,O) : 2 CH-(2C,O) : 1 CH_2-(C,O):2

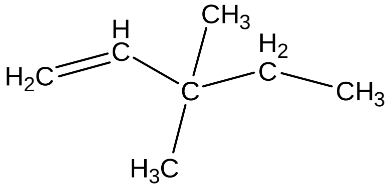
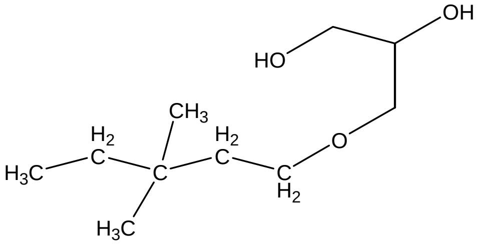
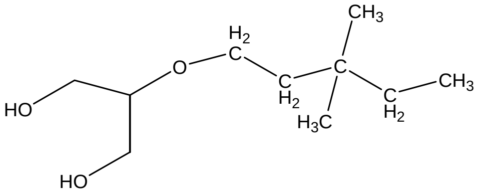
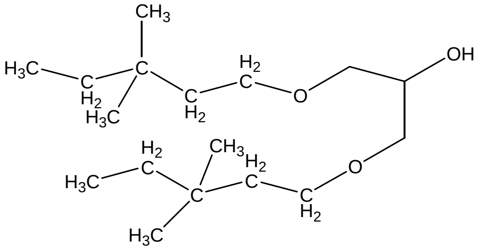
2,3-bis(1-methyl-1-isopropyl propoxy)-1-propanol		CH_3-(C) : 8 CH2-(2C) : 2 CH-(3C) : 2 O-(2C) : 2 OH-(C) : 1 C-(3C,O) : 2 CH-(2C,O) : 1 CH_2-(C,O):2
1,2,3-tris(1-methyl-1-isopropyl propoxy)-propane		CH_3-(C) : 12 CH2-(2C) : 3 CH-(3C) : 3 O-(2C) : 3 C-(3C,O) : 3 CH-(2C,O) : 1 CH_2-(C,O):2
2, 4-dimethyl-1-pentene		CH_3-(C) : 2 CH-(3C) : 1 =CH2 : 1 =C-(2C):1 CH3-(=C) :1 CH2-(C,=C):1
3-(1,1,3-tris methyl butoxy)-1,2-propanediol		CH_3-(C) : 4 CH2-(2C) : 1 CH-(3C) : 1 O-(2C) : 1 OH-(C) : 2 C-(3C,O) : 1 CH-(2C,O) : 1 CH_2-(C,O):2

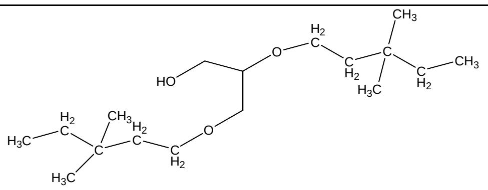
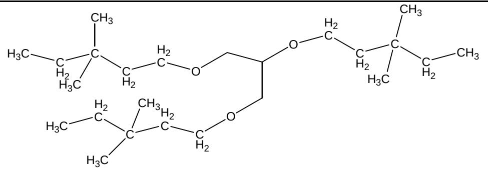
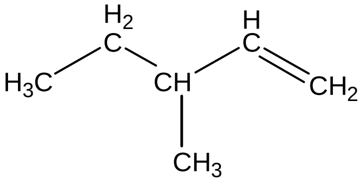
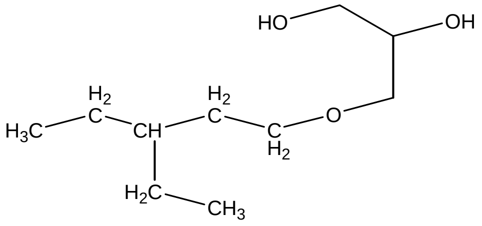
Name	Structure	Sub group
2-(1,1,3-tris methyl butoxy)-1,3-propanediol		CH_3-(C) : 4 CH2-(2C) : 1 CH-(3C) : 1 O-(2C) : 1 OH-(C) : 2 C-(3C,O) : 1 CH-(2C,O) : 1 CH_2-(C,O):2
1,3-bis(1,1,3-tris methyl butoxy)-2-propanol		CH_3-(C) : 8 CH2-(2C) : 2 CH-(3C) : 2 O-(2C) : 2 OH-(C) : 1 C-(3C,O) : 2 CH-(2C,O) : 1 CH_2-(C,O):2
2,3-bis(1,1,3-tris methyl butoxy)-1-propanol		CH_3-(C) : 8 CH2-(2C) : 2 CH-(3C) : 2 O-(2C) : 2 OH-(C) : 1 C-(3C,O) : 2 CH-(2C,O) : 1 CH_2-(C,O):2
1,2,3-tris(1,1,3-tris methyl butoxy)- propane		CH_3-(C) : 12 CH2-(2C) : 3 CH-(3C) : 3 O-(2C) : 3 C-(3C,O) : 3 CH-(2C,O) : 1 CH_2-(C,O):2

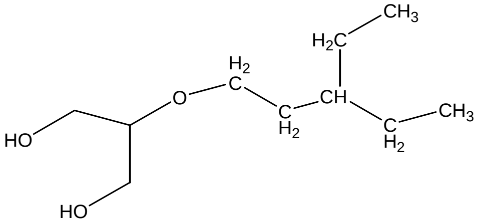
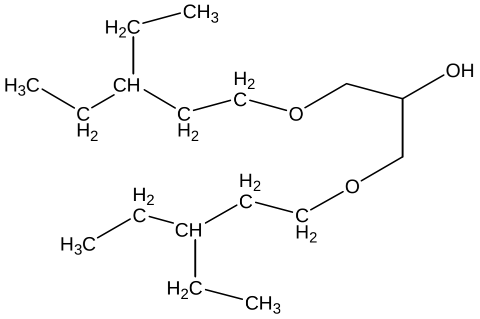
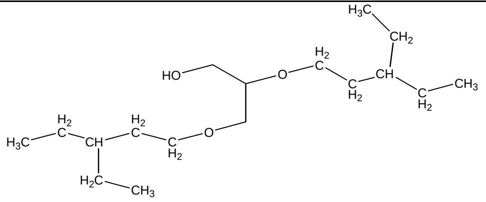
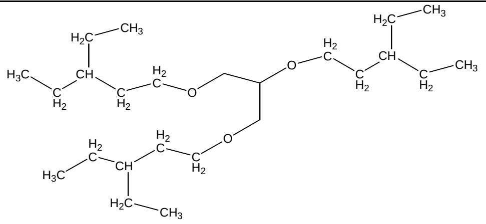
Name	Structure	Sub group
3-ethyl-2-pentene		CH3-(C) : 2 =C(C):1 =C-(2C): 1 CH3-(=C): 1 CH2-(C,=C):2
3-(1,1-diethyl propoxy)-1,2-propanediol		CH_3-(C) : 3 CH2-(2C) : 3 O-(2C) : 1 OH-(C) : 2 C-(3C,O) : 1 CH-(2C,O) : 1 CH_2-(C,O):2
2-(1,1-diethyl propoxy)-1,3-propanediol		CH_3-(C) : 3 CH2-(2C) : 3 O-(2C) : 1 OH-(C) : 2 C-(3C,O) : 1 CH-(2C,O) : 1 CH_2-(C,O):2
1,3-bis(1,1-diethyl propoxy)-2-propanol		CH_3-(C) : 6 CH2-(2C) : 6 O-(2C) : 2 OH-(C) : 1 C-(3C,O) : 2 CH-(2C,O) : 1 CH_2-(C,O):2

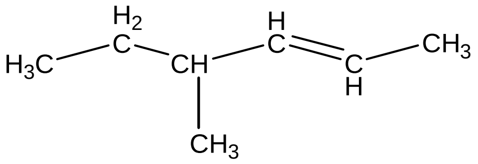
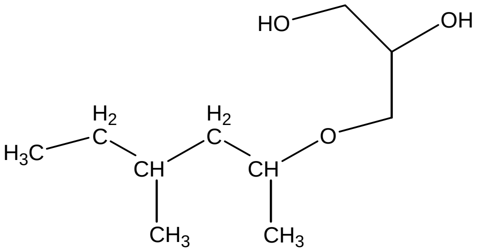
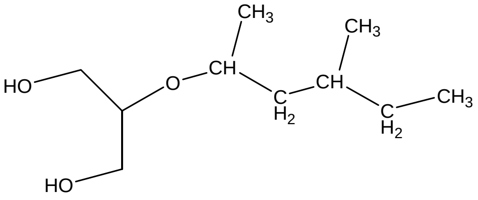
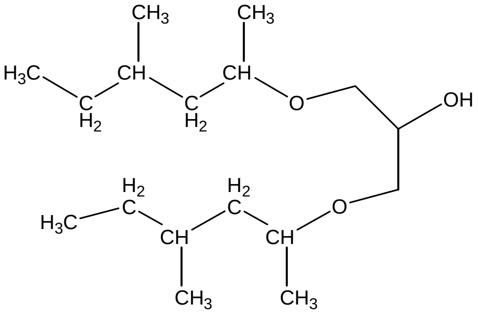
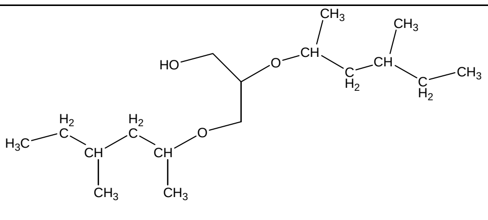
2,3-bis(1,1-diethyl propoxy)-1-propanol		CH_3-(C) : 6 CH2-(2C) : 6 O-(2C) : 2 OH-(C) : 1 C-(3C,O) : 2 CH-(2C,O) : 1 CH_2-(C,O):2
1,2,3-tris(1,1-diethyl propoxy)-propane		CH_3-(C) : 9 CH2-(2C) : 9 O-(2C) : 3 C-(3C,O) : 3 CH-(2C,O) : 1 CH_2-(C,O):2
Tran-2-methyl-3-hexene		CH_3-(C) :3 CH-(3C) :1 =CH-(C):2 CH2-(C,=C):1
3-(1-ethyl-3-methyl butoxy)-1,2-propanediol		CH_3-(C) : 3 CH2-(2C) : 2 CH-(3C) : 1 O-(2C) : 1 OH-(C) : 2 C-(3C,O) : 1 CH-(2C,O) : 1 CH_2-(C,O):2

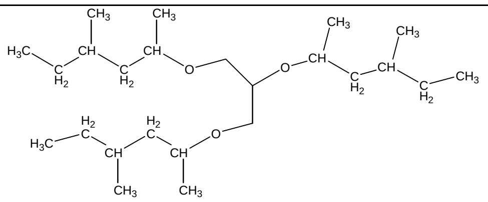
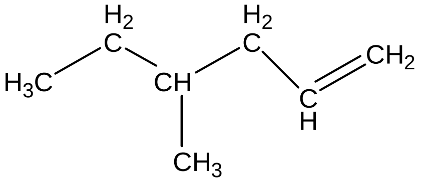
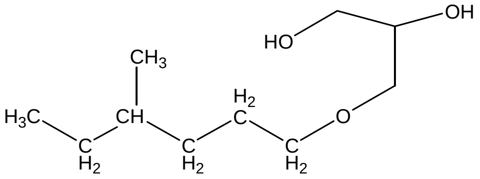
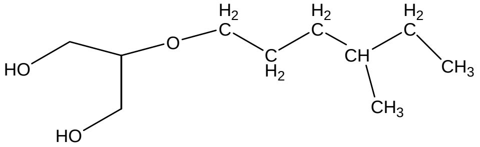
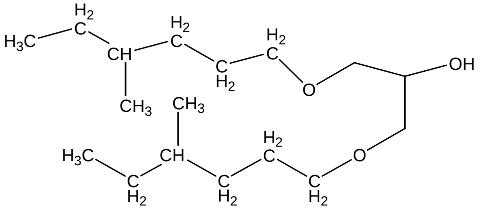
2-(1-ethyl-3-methyl butoxy)-1,3-propanediol		CH_3-(C) : 3 CH2-(2C) : 2 CH-(3C) : 1 O-(2C) : 1 OH-(C) : 2 C-(3C,O) : 1 CH-(2C,O) : 1 CH_2-(C,O):2
1,3-bis(1-ethyl-3-methyl butoxy)-2-propanol		CH_3-(C) : 6 CH2-(2C) : 4 CH-(3C) : 2 O-(2C) : 2 OH-(C) : 1 C-(3C,O) :2 CH-(2C,O) : 1 CH_2-(C,O):2
2,3-bis(1-ethyl-3-methyl butoxy)-1-propanol		CH_3-(C) : 6 CH2-(2C) : 4 CH-(3C) : 2 O-(2C) : 2 OH-(C) : 1 C-(3C,O) : 2CH-(2C,O) : 1 CH_2-(C,O):2
1,2,3-tris-(1-ethyl-3-methyl butoxy)- propane		CH_3-(C) : 9 CH2-(2C) : 6 CH-(3C) : 3 O-(2C) : 3 C-(3C,O) : 3 CH-(2C,O) : 1 CH_2-(C,O):2

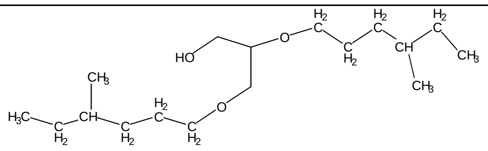
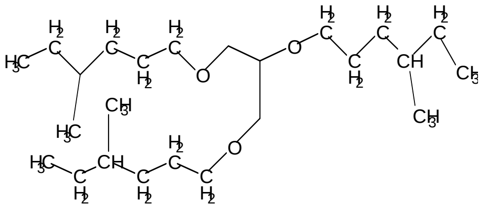
3,3-dimethyl-1-pentene		CH3-(C) :3 CH2-(2C):1 C-(4C) :1 =CH2 :1 =CH-(C) :1
3-(1,1-dimethyl pentoxy)-1,2-propanediol		CH$_3$-(C) : 3 CH2-(2C) : 2 C-(4C) : 1 O-(2C) : 1 OH-(C) : 2 C-(3C,O) : 1 CH-(2C,O) : 1 CH$_2$-(C,O):2
2-(1,1-dimethyl pentoxy)-1,3-propanediol		CH$_3$-(C) : 3 CH2-(2C) : 2 C-(4C) : 1 O-(2C) : 1 OH-(C) : 2 C-(3C,O) : 1 CH-(2C,O) : 1 CH$_2$-(C,O):2
1,3-bis(1,1-dimethyl pentoxy)-2-propanol		CH$_3$-(C) : 6 CH2-(2C) : 4 C-(4C) : 2 O-(2C) : 2 OH-(C) : 1 C-(3C,O) : 2 CH-(2C,O) : 1 CH$_2$-(C,O):2

2,3-bis(1,1-dimethyl pentoxy)-1-propanol		CH_3-(C) : 6 CH2-(2C) : 4 C-(4C) : 2 O-(2C) : 2 OH-(C) : 1 C-(3C,O) : 2 CH-(2C,O) : 1 CH_2-(C,O):2
1,2,3-tris-(1,1-dimethyl pentoxy)- propane		CH_3-(C) : 9 CH2-(2C) : 6 C-(4C) : 3 O-(2C) : 3 C-(3C,O) : 3 CH-(2C,O) : 1 CH_2-(C,O):2
3-methyl-1-pentene		CH3-(C) :2 CH2-(2C):1 CH-(3C) :1 =CH2 :1 =CH-(C) :1
3-(1-methyl-2-ethyl-butoxy)-1,2-propanediol		CH_3-(C) : 2 CH2-(2C) : 3 CH-(3C) : 1 O-(2C) : 1 OH-(C) : 2 CH-(2C,O) : 1 CH_2-(C,O):2

Name	Structure	Sub group
2-(1-methyl-2-ethyl-butoxy)-1,3-propanediol		CH_3-(C) : 2 CH2-(2C) : 3 CH-(3C) : 1 O-(2C) : 1 OH-(C) : 2 CH-(2C,O) : 1 CH_2-(C,O):3
1,3-bis(1-methyl-2-ethyl-butoxy)-2-propanol		CH_3-(C) : 4 CH2-(2C) : 6 CH-(3C) : 2 O-(2C) : 2 OH-(C) : 1 CH-(2C,O) : 1 CH_2-(C,O):4
2,3-bis(1-methyl-2-ethyl-butoxy)-1-propanol		CH_3-(C) : 4 CH2-(2C) : 6 CH-(3C) : 2 O-(2C) : 2 OH-(C) : 1 CH-(2C,O) : 1 CH_2-(C,O):4
1,2,3-tris-(1-methyl-2-ethyl-butoxy)- propane		CH_3-(C) : 6 CH2-(2C) : 9 CH-(3C) : 3 O-(2C) : 3 CH-(2C,O) : 1 CH_2-(C,O):5

Cis-5-methyl-2-hexene		CH3-(C) :3 CH-(3C) :1 =CH-(C) :1 CH2-(2C) :2
3-(1,3-dimethyl-pentoxy)-1,2-propanediol		CH_3-(C) : 3 CH2-(2C) : 2 CH-(3C) : 1 O-(2C) : 1 OH-(C) : 2 CH-(2C,O) : 1 CH_2-(C,O):2
2-(1,3-dimethyl-pentoxy)-1,3-propanediol		CH_3-(C) : 3 CH2-(2C) : 2 CH-(3C) : 1 O-(2C) : 1 OH-(C) : 2 CH-(2C,O) : 1 CH_2-(C,O):2
1,3-bis(1,3-dimethyl-pentoxy)-2-propanol		CH_3-(C) : 6 CH2-(2C) : 4 CH-(3C) : 2 O-(2C) : 2 OH-(C) : 1 CH-(2C,O) : 2 CH_2-(C,O):2
2,3-bis(1,3-dimethyl-pentoxy)-1-propanol		CH_3-(C) : 6 CH2-(2C) : 4 CH-(3C) : 2 O-(2C) : 2 OH-(C) : 1 CH-(2C,O) : 2 CH_2-(C,O):2

1,2,3-tris-(1,3-dimethyl-pentoxy)- propane		CH_3-(C) : 9 CH2-(2C) : 6 CH-(3C) : 3 O-(2C) : 3 CH-(2C,O) : 3 CH_2-(C,O):2
4-methyl-1-hexene		CH3-(C) :2 CH-(3C) :1 =CH-(C) :1 CH2-(2C) :2 =CH2 : 1
3-(4-methyl-hexoxy)-1,2-propanediol		CH_3-(C) : 2 CH2-(2C) :3 CH-(3C) : 1 O-(2C) : 1 OH-(C) : 2 CH-(2C,O) : 1 CH_2-(C,O):3
2-(4-methyl-hexoxy)-1,3-propanediol		CH_3-(C) : 2 CH2-(2C) :3 CH-(3C) : 1 O-(2C) : 1 OH-(C) : 2 CH-(2C,O) : 1 CH_2-(C,O):3
1,3-bis(4-methyl-hexoxy)-2-propanol		CH_3-(C) : 4 CH2-(2C) :6 CH-(3C) : 2 O-(2C) : 2 OH-(C) : 1 CH-(2C,O) : 1 CH_2-(C,O):4

2,3-bis(4-methyl-hexoxy)-1-propanol		CH_3-(C) : 4 CH2-(2C) :6 CH-(3C) : 2 O-(2C) : 2 OH-(C) : 1 CH-(2C,O) : 1 CH_2-(C,O):4
1,2,3-tris-(4-methyl-hexoxy)-propane		CH_3-(C) : 6 CH2-(2C) :9 CH-(3C) : 3 O-(2C) : 3 CH-(2C,O) : 1 CH_2-(C,O):5

Note: Benson's subgroup (Aspen subgroup ID) will be listed below;

C-(C)(H)3 (100), C-(C)2(H)2 (101), C-(C)3(H) (102),
C-(C)4 (103), CD-(H)2 (104), CD-(C)(H) (105),
C-(CD)(H)3 (115), C-(CD)(H)2 (116), C-(CD)(C)(H)2 (117),
C-(CD)(C)3 (118), C-(CD)(C)(H)2 (119), C-(CD)(C)2(H) (120),
C-(CD)2(C)(H), alkane Gauche (145), cis- (147),
cycopentane (153), cyclopentene (154), cyclohexane (156),
cyclohexene (157), O-(C)2 (188), O-(C)(H) (189),
C-(O)(C)3 (209), C-(O)(C)2(H) (210), C-(O)(C)(H)2 (211),
C-(O)(H)3 (212) ether, oxygen, gauche (213

APPENDIX D

SIMULATION PROCEDURE

This chapter will be described the Simulation procedure for study of the etherification reaction of reactive olefins with ethanol using the Gibbs reactor. It is explained the step detail for added the components that not exist in data bank in Aspen plus program.

1. To start Aspen plus program follow this step;

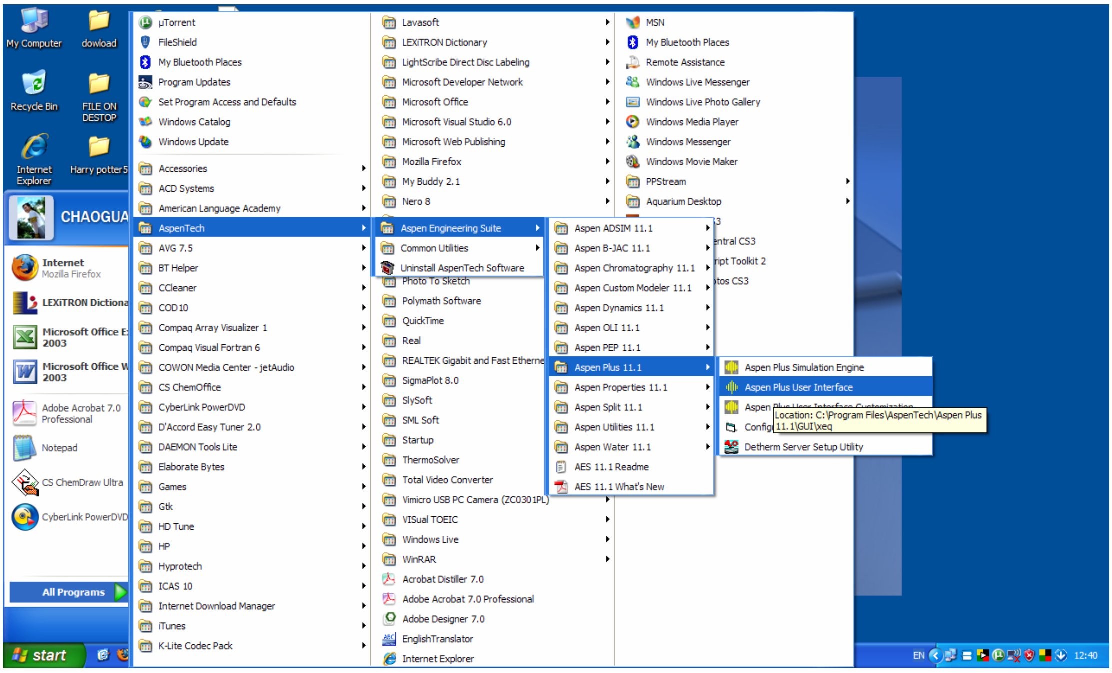
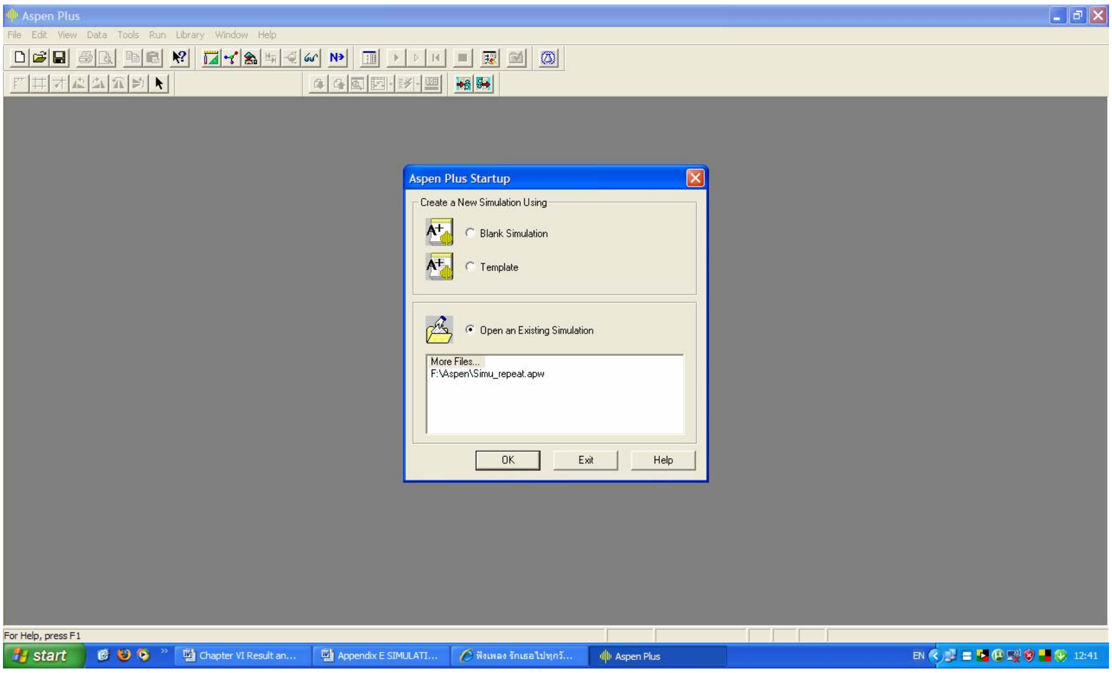


Figure E-1 Open the Aspen plus program.

1.1 Click start, and then point to program

1.2 Point to Aspen tech, point to AspenTech, point to Aspen Plus and then click Aspen Plus user interface.



○ Blank Simulation
○ Template
● Open an Existing Simulation

More Files...
F:\Aspen\Simu_repeat.apw

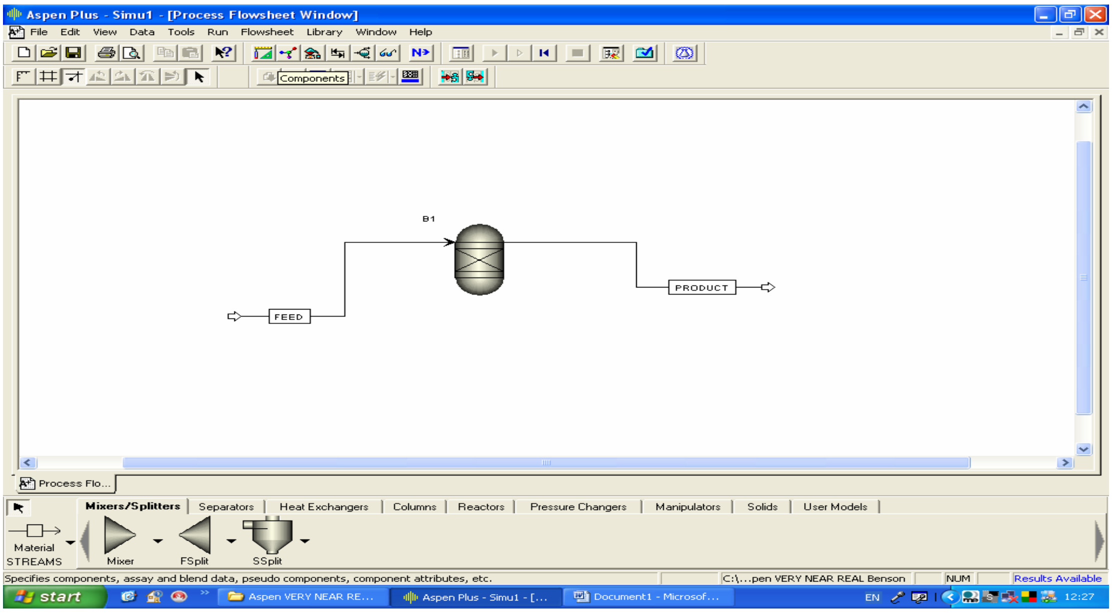
Figure E-2 Choose type of open the Aspen plus program.

In the startup dialog box, choose whether you want to create a new simulation using a blank simulation or a template, or open an existing simulation. If you choose to create a new run from a template, you will be prompted to specify the template and run type for the new run. Perform the remaining steps only if you are opening an exist run.

1. To open an existing simulation, either selects the filename from the list in the startup dialog, or selects more files, and click OK. If you select a file from the startup dialog, the aspen plus main window appears with the chosen file displayed. If you choose more files, the open dialog box appears. Perform the remaining steps only if you choose more files.
2. In the open dialog box, in the files of type box, select the file format in which the run was saved. For example, Aspen Plus document format (.apw) or backup file format (.bkp).
3. Use the look in list box to locate the directory where the file is stored, and then click the file you want to open, and click open.

2. Added the new component to Aspen plus data bank.

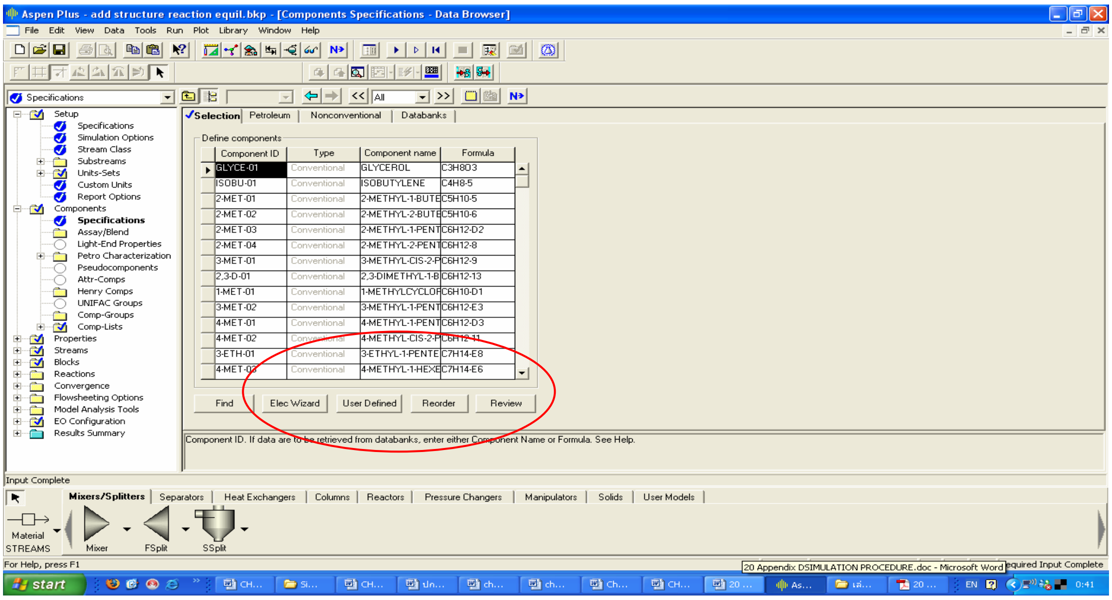
The procedures of using Aspen plus to simulate follow this research. To explanations the step by step to add the new components to Aspen plus program databank are listed below.



Specifies components, assay and blend data, pseudo components, component attributes, etc.

Figure E-3 Data browser of Aspen plus program.

2.1 Click the data browser to get the tree menu.

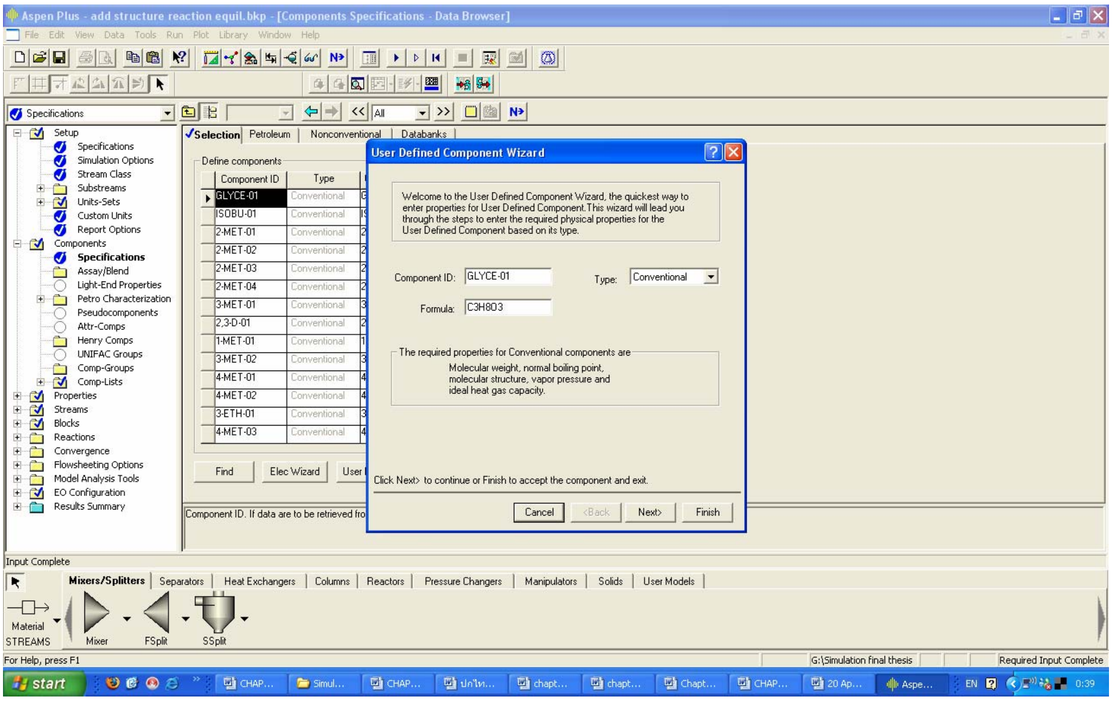


Component ID	Type	Component name	Formula
GLYCE-01	Conventional	GLYCEROL	C3H8O3
ISOBU-01	Conventional	ISOBUTYLENE	C4H8-5
2-MET-01	Conventional	2-METHYL-1-BUTE	C5H10-5
2-MET-02	Conventional	2-METHYL-2-BUTE	C5H10-6
2-MET-03	Conventional	2-METHYL-1-PENT	C6H12-D2
2-MET-04	Conventional	2-METHYL-2-PENT	C6H12-8
3-MET-01	Conventional	3-METHYL-CIS-2-P	C6H12-9
2,3-D-01	Conventional	2,3-DIMETHYL-1-B	C6H12-13
1-MET-01	Conventional	1-METHYLCYCLOF	C6H10-D1
3-MET-02	Conventional	3-METHYL-1-PENT	C6H12-E3
4-MET-01	Conventional	4-METHYL-1-PENT	C6H12-D3
4-MET-02	Conventional	4-METHYL-CIS-2-P	C6H12-11
3-ETH-01	Conventional	3-ETHYL-1-PENTE	C7H14-E8
4-MET-03	Conventional	4-METHYL-1-HEXE	C7H14-E6

Component ID. If data are to be retrieved from databanks, enter either Component Name or Formula. See Help.

Figure E-4 Tab for User defines new component.

2.2 In specification menu, click selection tab and then click the User define to identify the formula and the name of new component and then click finish.



Define components

Component ID	Type
GLYCE-01	Conventional
ISOBU-01	Conventional
2-MET-01	Conventional
2-MET-02	Conventional
2-MET-03	Conventional
2-MET-04	Conventional
3-MET-01	Conventional
2,3-D-01	Conventional
1-MET-01	Conventional
3-MET-02	Conventional
4-MET-01	Conventional
4-MET-02	Conventional
3-ETH-01	Conventional
4-MET-03	Conventional

Welcome to the User Defined Component Wizard, the quickest way to enter properties for User Defined Component. This wizard will lead you through the steps to enter the required physical properties for the User Defined Component based on its type.

Component ID: GLYCE-01
Type: Conventional
Formula: C3H8O3

The required properties for Conventional components are
Molecular weight, normal boiling point, molecular structure, vapor pressure and ideal heat gas capacity.

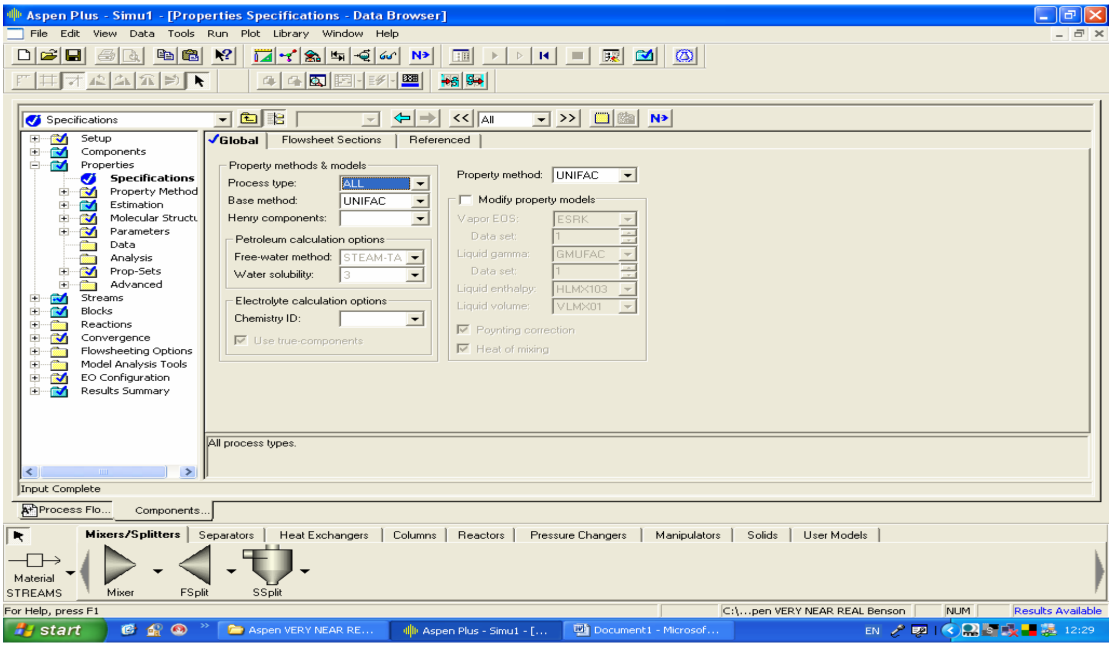
Click Next> to continue or Finish to accept the component and exit.

Component ID. If data are to be retrieved fro

Input Complete

Figure E-5 Define new components.

2.3 Type the formula and name of new components.



Property methods & models
Process type: ALL
Base method: UNIFAC
Henry components:

Petroleum calculation options
Free-water method: STEAM-TA
Water solubility: 3

Electrolyte calculation options
Chemistry ID:
☑ Use true-components

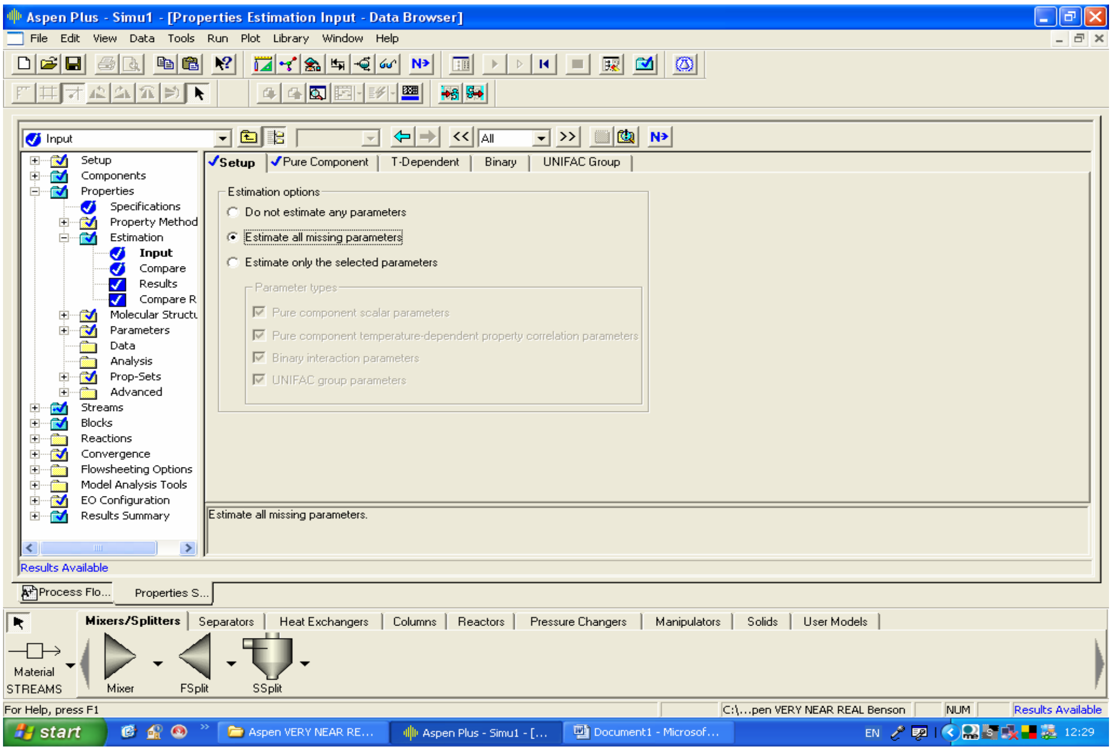
Property method: UNIFAC
☐ Modify property models
Vapor EOS: ESRK
Data set: 1
Liquid gamma: GMUFAC
Data set: 1
Liquid enthalpy: HLMX103
Liquid volume: VLMX01
☑ Poynting correction
☑ Heat of mixing

All process types.

Input Complete

Figure E-6 Specification of thermodynamic method.

2.4 In specification properties, choose the thermodynamic properties.



Estimation options

○ Do not estimate any parameters

● Estimate all missing parameters

○ Estimate only the selected parameters

Parameter types

☑ Pure component scalar parameters

☑ Pure component temperature-dependent property correlation parameters

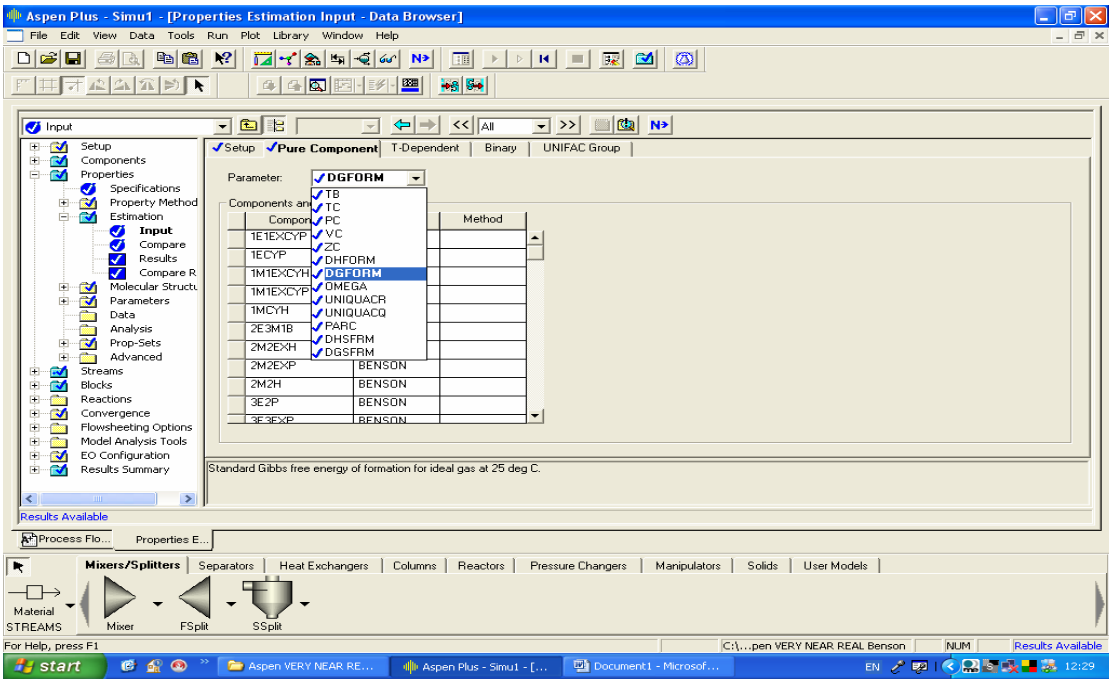
☑ Binary interaction parameters

☑ UNIFAC group parameters

Estimate all missing parameters.

Figure E-7 Click Estimate of missing parameters.

2.5 Estimation tab, tick Estimate all missing parameters.



Parameter: DGFORM

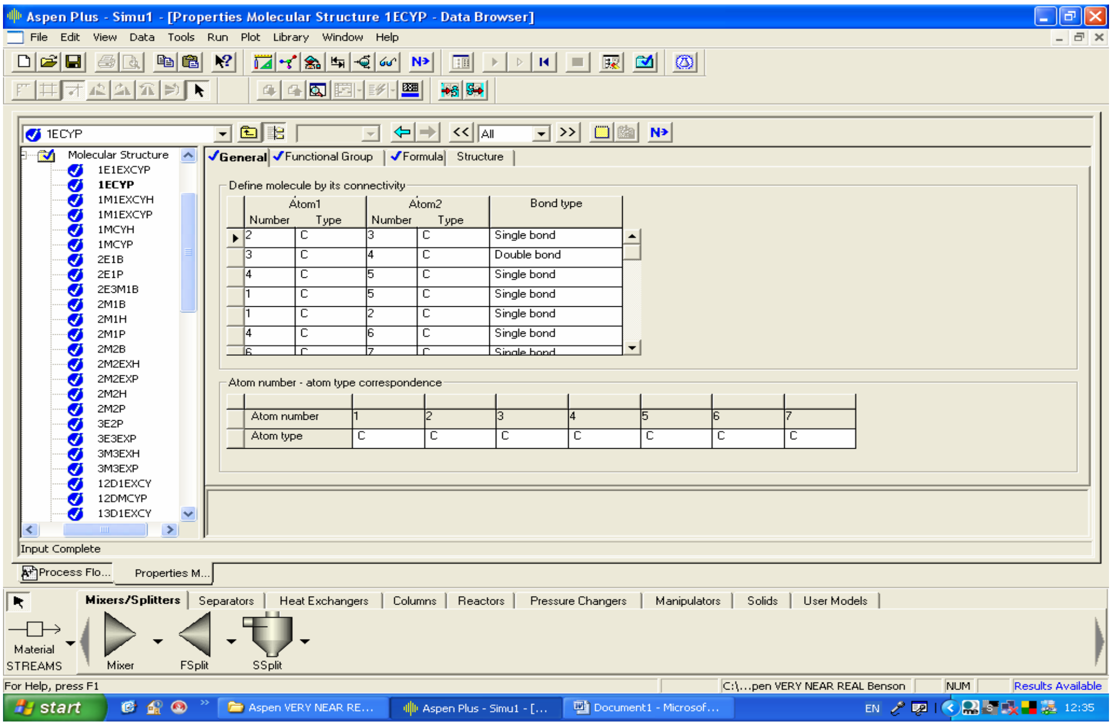
Components and methods

Component	Method
1E1EXCYP	
1ECYP	
1M1EXCYH	
1M1EXCYP	
1MCYH	
2E3M1B	
2M2EXH	
2M2EXP	BENSON
2M2H	BENSON
3E2P	BENSON
3E3EXP	BENSON

Standard Gibbs free energy of formation for ideal gas at 25 deg C.

Figure E-8 Specification of properties for estimate.

2.6 Pure component tab, choose the properties that you want to estimate.



Aspen Plus - Simu1 - [Properties Molecular Structure 1ECYP - Data Browser]

1ECYP

General | Functional Group | Formula | Structure

Define molecule by its connectivity

Atom1 Number	Atom1 Type	Atom2 Number	Atom2 Type	Bond type
2	C	3	C	Single bond
3	C	4	C	Double bond
4	C	5	C	Single bond
1	C	5	C	Single bond
1	C	2	C	Single bond
4	C	6	C	Single bond
6	C	7	C	Single bond

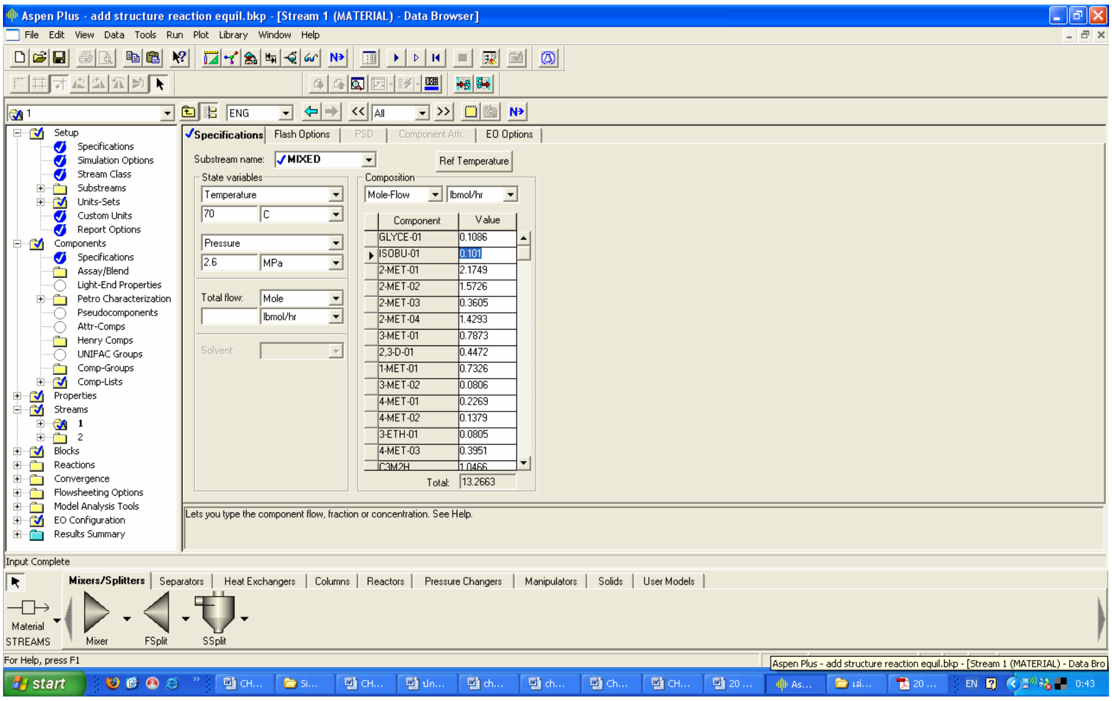
Atom number - atom type correspondence

Atom number	1	2	3	4	5	6	7
Atom type	C	C	C	C	C	C	C

Input Complete

Figure E-9 Defins detail of new component.

2.7 Molecular structure tab, added general structure, functional group, formula and structure- the molecular structure can be imported from other program that type mole file (.mol).



Aspen Plus - add structure reaction equil.bkp - [Stream 1 (MATERIAL) - Data Browser]

Specifications | Flash Options | PSD | Component Attr. | EO Options

Substream name: MIXED

State variables

Temperature: 70 C

Pressure: 2.6 MPa

Total flow: Mole, lbmol/hr

Composition: Mole-Flow, lbmol/hr

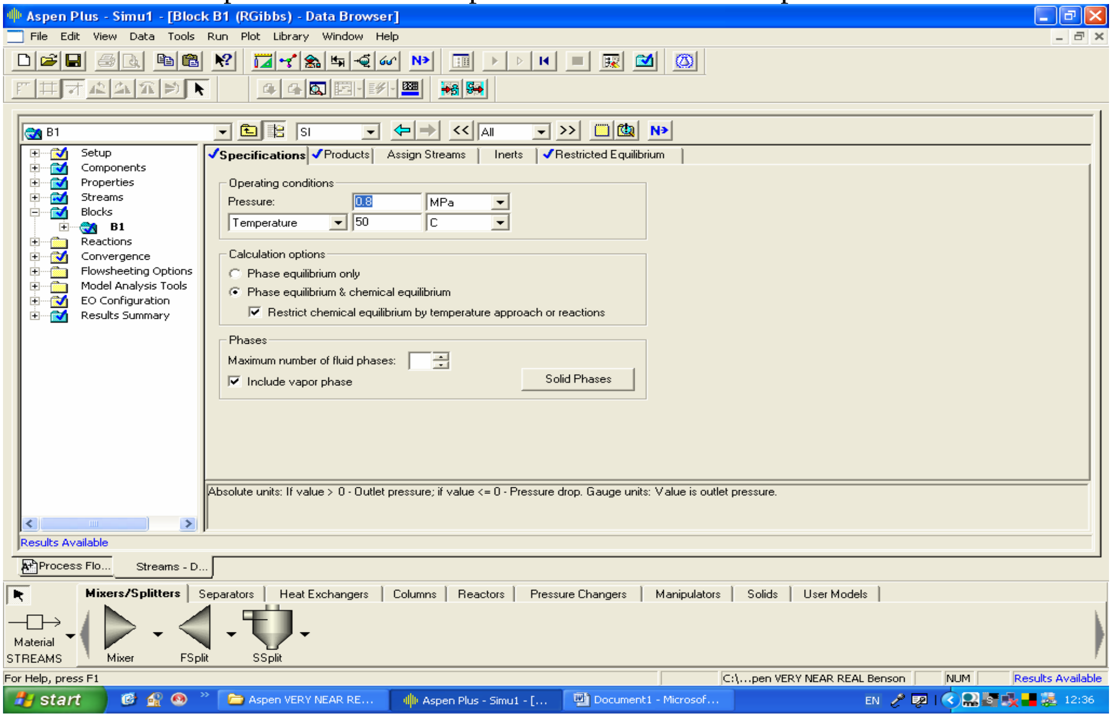
Component	Value
GLYCE-01	0.1086
ISOBU-01	0.101
2-MET-01	2.1749
2-MET-02	1.5726
2-MET-03	0.3605
2-MET-04	1.4293
3-MET-01	0.7873
2,3-D-01	0.4472
1-MET-01	0.7326
3-MET-02	0.0806
4-MET-01	0.2269
4-MET-02	0.1379
3-ETH-01	0.0805
4-MET-03	0.3951
C3M2H	1.0466
Total:	13.2663

Lets you type the component flow, fraction or concentration. See Help.

Input Complete

Figure E-10 Specification of feed stream.

2.8 This step showed that the specification of feed components.



Operating conditions

Pressure: 0.8 MPa

Temperature 50 C

Calculation options

○ Phase equilibrium only

● Phase equilibrium & chemical equilibrium

☑ Restrict chemical equilibrium by temperature approach or reactions

Phases

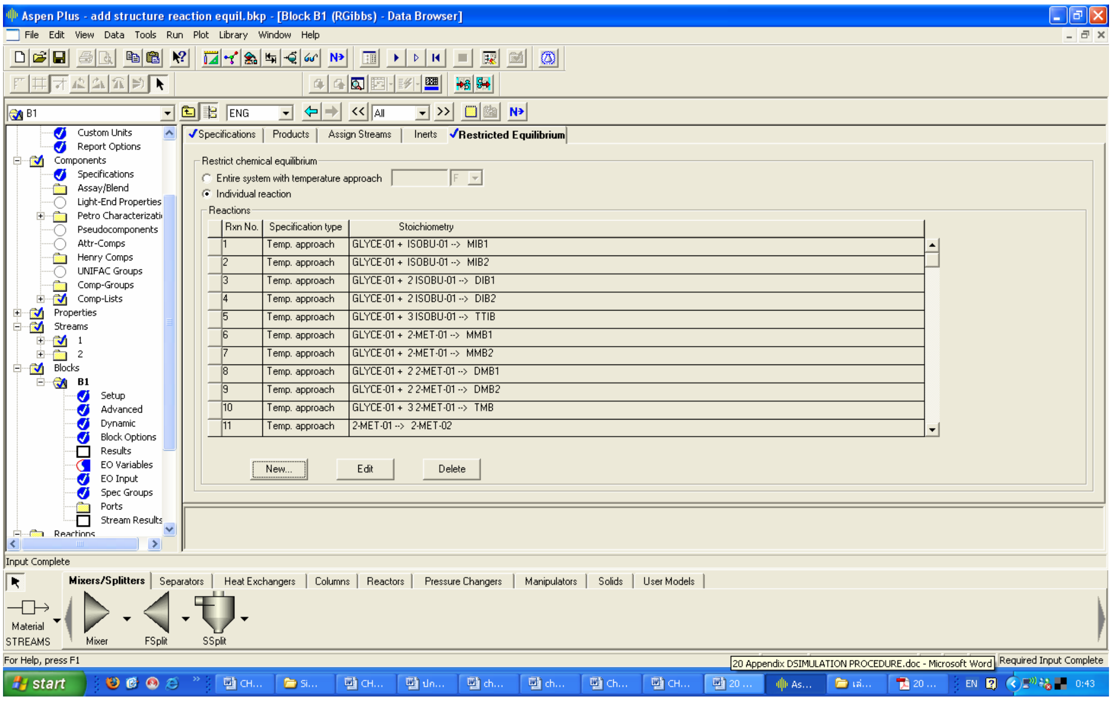
Maximum number of fluid phases:

☑ Include vapor phase

Absolute units: If value > 0 - Outlet pressure; if value <= 0 - Pressure drop. Gauge units: Value is outlet pressure.

Figure E-11 Specification the operating condition.

2.9 Next step, you must specify the conditions at reactor.



Restrict chemical equilibrium

○ Entire system with temperature approach F

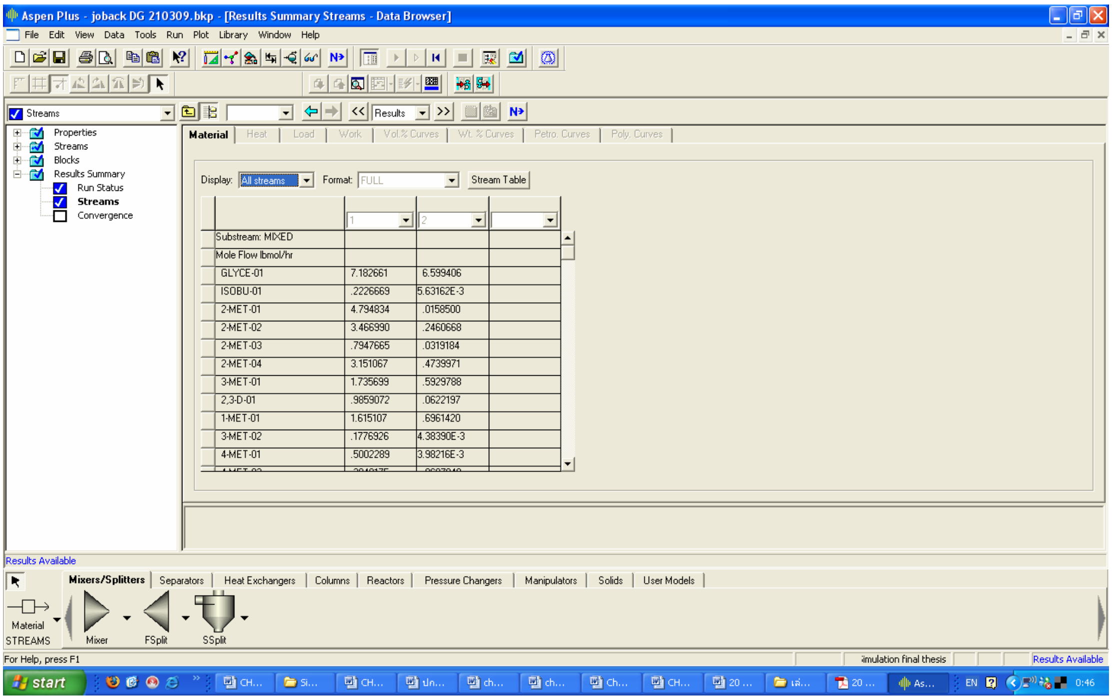
● Individual reaction

Reactions

Rxn No.	Specification type	Stoichiometry
1	Temp. approach	GLYCE-01 + ISOBU-01 --> MIB1
2	Temp. approach	GLYCE-01 + ISOBU-01 --> MIB2
3	Temp. approach	GLYCE-01 + 2 ISOBU-01 --> DIB1
4	Temp. approach	GLYCE-01 + 2 ISOBU-01 --> DIB2
5	Temp. approach	GLYCE-01 + 3 ISOBU-01 --> TTIB
6	Temp. approach	GLYCE-01 + 2-MET-01 --> MMB1
7	Temp. approach	GLYCE-01 + 2-MET-01 --> MMB2
8	Temp. approach	GLYCE-01 + 2 2-MET-01 --> DMB1
9	Temp. approach	GLYCE-01 + 2 2-MET-01 --> DMB2
10	Temp. approach	GLYCE-01 + 3 2-MET-01 --> TMB
11	Temp. approach	2-MET-01 --> 2-MET-02

Figure E-12 Define reactions.

2.10 The reaction that can be occurred in reactor are showed.



Display: All streams Format: FULL

	1	2	
Substream: MIXED			
Mole Flow lbmol/hr			
GLYCE-01	7.182661	6.599406	
ISOBU-01	.2226669	5.63162E-3	
2-MET-01	4.794834	.0158500	
2-MET-02	3.466990	.2460668	
2-MET-03	.7947665	.0319184	
2-MET-04	3.151067	.4739971	
3-MET-01	1.735699	.5929788	
2,3-D-01	.9859072	.0622197	
1-MET-01	1.615107	.6961420	
3-MET-02	.1776926	4.38390E-3	
4-MET-01	.5002289	3.98216E-3	

Figure E-13 Checked results.

2.11 Finally, the result will show the component in each stream.

VITAE

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Utilization of Glycerol as a Fuel Extender by Etherified with FCC Gasoline

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Abstract

Glycerol, a by-product of biodiesel production was employed as the fuel extender in this study. The process was investigated by etherifying the entire fluidized catalytic cracking (FCC) gasoline with glycerol (99.5% purity) catalyzed by commercial catalyst i.e., Amberlyst 15, Amberlyst 16 and β-zeolite. The reactions were carried out in a pressurized liquid phase reactor at 70 °C and 2.6 MPa with a molar ratio of FCC gasoline to glycerol ratio of 4:1 for 10 h. FCC gasoline is a potential valuable feedstock of reactive olefins for production of oxygenated ethers. On the contrary, these olefinic compounds should be diminished also in order to meet the new mandatory of gasoline composition which allows the olefin content not to exceed 18 vol% as regulated by Euro 4 standard. The properties of FCC and etherified FCC products were determined by the standard analysis of Research Octane Number (RON), blending Reid vapor pressure (bRvp), distillation temperature following the standard methods of ASTM D -2699, ASTM D 5191-99 and ASTM D 86-05, respectively. The process of FCC gasoline etherification with glycerol has several benefits. Ethers produced from glycerol which considered as renewable could extend the gasoline volume. The etherified gasoline product has lower blending Reid vapor pressure (bRvp). The loss of octane number due to olefin reduction could be compensated by in situ ether production.

Keywords: Renewable energy, glycerol, etherification, FCC gasoline.

1. Introduction

Nowadays global warming and energy crisis are recognized as the most global severe problems. The transportation might be a significant part of the concern. Biodiesel is an alternative fuel that is produced by chemically reacting a vegetable oil or animal fat with an alcohol such as methanol or ethanol. An advantage of biodiesel is that it is “carbon neutral” in terms of CO_2 since the CO_2 has recently come from the atmosphere through fixation by planting. However, for every 9 kg of biodiesel produced, about 1 kg of a crude glycerol by-product is formed (Dasari et al., 2005). As the biodiesel production is increasing exponentially, the crude glycerol generated from the transesterification has also been generated in a large quantity carrying thus an oversupply.

Etherification of glycerol is one of promising process for oxygenate fuel production. However, until now the research works are limited with only two etherification agents isobutylene (IB) and tert-butyl alcohol (TBA) for the etherification with glycerol (Noureddini and Harmeier, 1998), (Klepacova et al., 2005; Klepacova et al., 2006),(Karinen and Krause, 2006). Isobutylene reacts with glycerol of acid catalyst and a mixture of mono-, di- and tri-tert-butyl ethers of glycerol is formed. Higher glycerol ether mainly di- and tri-tert-butyl ethers could be similar as the current commercial oxygenate additive used as oxygenates to gasoline. Furthermore, addition of these ethers has positive effect on the quality of gasoline and preferentially ethers are active by reduction of fumes and particulate matters, carbon oxides and carbonyl compounds in exhaust.

FCC gasoline contained many C_4-C_8 reactive olefins e.g. IB, isoamylene (IA) which is a promising source for etherification. On the contrary, these olefins content should be eliminated or minimized before using as a gasoline in the environment viewpoint. The etherification of entire FCC gasoline have been successful experimented with methanol (Pescarollo et al., 1993) and ethanol (Kiatkittipong et al., 2008, 2009). The etherification of FCC light gasoline with methanol was firstly studied by Pescarollo et al., 1993. Kiatkittipong et al., 2008 studied etherification of FCC gasoline with ethanol catalyzed by commercial catalysts, i.e., Amberlyst 16 and β-zeolite. Comparing between two catalysts, β-zeolite was a more suitable catalyst for the etherification of FCC gasoline with ethanol because not only a better catalytic activity for etherification, but some isomerization also occurs without aromatization. It offered products with higher RON and ethanol conversion with lower bRvp. A satisfied drivability index showed the cold start problem might not be occurred even in low bRvp (Kiatkittipong et al., 2009).

In this study, the process was investigated by etherifying the entire FCC gasoline with glycerol catalyzed by commercial catalysts, i.e., Amberlyst 16, Amberlyst 15 and β-zeolite. The suitable operating conditions (temperature, amount of catalysts) were primarily screened. The properties of etherified gasoline product, i.e., RON, bRvp and distillation temperature were compared with original FCC gasoline.

2. Experimental

2.1 Chemicals

FCC gasoline is cut off from a catalytic cracking unit of an oil refinery. Glycerol grade AR (99.5 vol. %) from QRëC.

2.2 Catalysts

Amberlyst 16, Amberlyst 15 and β-zeolite used in this study were purchased from Chemica Fluka and Tosoh (Japan), respectively. The catalysts were dried overnight in an oven at 110°C before use. The physical properties of the catalysts were shown in Table 1.

Table 1: Physical properties of catalysts

	Surface area (m^2/g)	Particle size (μm)	Pore diameter (nm)	Pore volume (cm^2/g)
Amberlyst 16	45	700	20	1.82
Amberlyst 15	53	600-850	30	0.40
Beta-zeolite	625	45	0.58	0.129

2.3 Apparatus

Etherification of FCC gasoline with glycerol was carried out in a cylindrical shape autoclave reactor as shown in Fig. 1. The volume of reactor was 100 cm^3 with reactor height of 8 cm and outside and inside diameters of 5 and 4 cm, respectively. The turbine was used to stir the mixture. A valve for liquid sampling and a port for the thermocouple were installed at the top. The mixture was stirred by using turbine at the maximum speed of 1163 rpm for all experiments. At this speed, the effect of external mass transfer resistance could be neglected. The reactor was maintained at a constant temperature by circulating hot water in jackets.

2.4 Analysis

The standard analysis of Research Octane Number (RON), blending Reid vapor pressure (bRvp) and distillation temperature were carried out by following the standard methods of following the standard methods of ASTM D -2699, ASTM D 5191-99 and ASTM D 86-05, respectively

2.5 Operation procedure

The reaction system consisted of 84 cm^3 of FCC gasoline, 16 cm^3 of glycerol and 10 g of catalyst and was carried out at 70 °C for 10 h under a pressure of 2.6 MPa. After run, the reactor was cooled down to a room temperature before opening the reactor and collecting the sample in order to prevent the evaporation loss

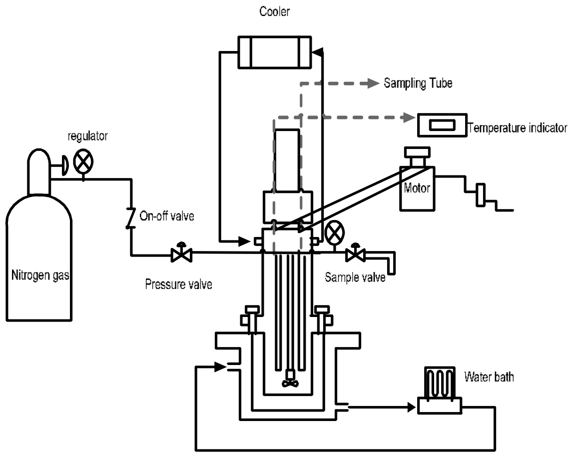

Figure1: Schematic diagram of the experimental apparatus

3. Results and Discussions

3.1 Catalyst and operating condition screening

3.1.1 Catalyst screening

Among three acidic catalysts (i.e., Amberlyst 16, Amberlyst 15 and β-zeolite), only Amberlyst 16 gives a complete conversion of glycerol after 10 hours of reaction. Therefore Amberlyst 16 was selected as a suitable catalyst for the reaction.

3.1.2 The influence of the amount of catalyst

The amounts of Amberlyst 16 catalyst were varied for 0.5, 5 and 10 g. With Amberlyst 16 less than 10 g, glycerol could not be converted completely (results were not shown here).

3.1.3 The influence of operating temperature

Etherification of glycerol catalyzed by Amberlyst 16 were carried out in the temperature range of 50-70° C. Glycerol conversion increased with increasing operating temperature from 50° C to 70° C. It should be noted that glycerol could be completely converted within 10 hours with the operating temperature of 70° C.

3.2 Characterization of etherification products and FCC gasoline

Research Octane number (RON) and blending Reid vapor pressure (bRvp) of etherification products analyzed were shown in Table2.

Table 2: Comparison of gasoline properties

	FCC gasoline	Etherified FCC gasoline with glycerol
RON	88	90.1
bRvp (psia)	6.5	4.5
Density (g/cm^3)	0.7186	0.7403

The results show that RON of etherified FCC gasoline is higher than that of original FCC gasoline. This implies that the RON of ethers product might be higher than that of olefinic compounds which were consumed in the reaction. The bRvp of etherified FCC decrease form 6.5 psia to 4.5 psia. The reduction of bRvp is beneficial especially for hot countries or in summer. It should be noted that the increase of RON in case of etherified with glycerol are different from ethanol. In our previous study Kiatkittipong et at. 2008, FCC gasoline was etherified with 20 vol% ethanol catalyzed by β-zeolite and RON of 94.1 could be obtained. Since the unreacted ethanol can be left in the gasoline therefore the RON of the etherified product also influenced by ethanol which have high octane ($RON_{ethanol}$ = 118). However, in the case of glycerol, glycerol could not be remaining in the gasoline. Therefore, the RON improvement might be only due to the etherification with glycerol. On the contrary, the bRvp of etherified FCC with glycerol are lower than that of etherified with 20 % vol ethanol. This is due to high bRvp of ethanol remaining in the gasoline.

Figure 2 shows distillation curve of original FCC gasoline and etherified FCC gasoline with glycerol. Etherified FCC gasoline with glycerol showed higher distillation temperature than that of original FCC gasoline. The results might support the decreasing of the bRvp of etherified product as previously shown in Table 2.

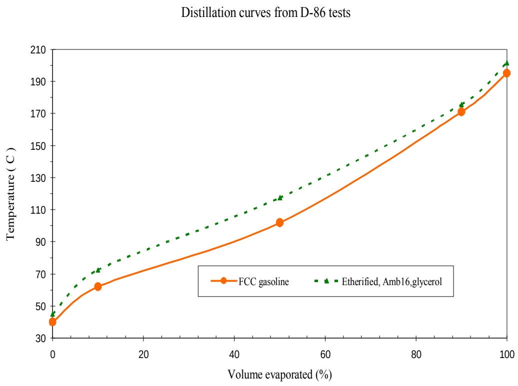

Figure2: Distillation curve from D-86 Tests

4. Conclusion

The etherification of FCC gasoline with glycerol showed a promising process for gasoline quality improvement and utilization of glycerol as a fuel extender simultaneously. The etherified FCC gasoline showed higher research octane number (RON) and lower blending Reid vapor pressure (bRvp) which are preference properties. The suitable operating condition of reaction were carried out by feeding FCC to glycerol ratio of 4:1 with operating temperature of 70°C, 10 g of Amberlyst 16 catalyst and 10 hours of reaction time.

5. Acknowledgement

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