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THERMODYNAMIC STUDY OF ETHERIFICATION REACTIONS BETWEEN GASOLINE FROM FLUIDIZED CATALYTIC CRACKING AND ETHANOL

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งานวิจัยนี้ศึกษาอุณหพลศาสตร์ของปฏิกิริยาอีเทอริฟิเคชันระหว่างแก๊สโซลีนจากฟลูอิไดซ์คะตะไลติกแครกกิงกับเอทานอลโดยการใช้โปรแกรมจำลองแอสเพนพลัส เวอร์ชัน 11.1 องค์ประกอบของแก๊สโซลีนประกอบด้วยช่วงคาร์บอนอะตอม 4-7 อะตอม วิธีกรุ๊ปคอนทริบิวชัน (เช่น วิธีแอมบรอส วิธีโจแบค วิธีกานี และวิธีเบนสัน) ถูกนำมาใช้ประมาณค่าตัวแปรที่หายไป (เช่น ดันวิกฤต อุณหภูมิวิกฤต จุดเดือด ค่าพลังงานอิสระการก่อเกิดสารที่สภาวะมาตรฐาน) ในขั้นต้นจากการเลือกวิธีกรุ๊ปคอนทริบิวชัน พบว่าวิธีของกานีและวิธีของโจแบคสามารถทำนายได้ดีสำหรับ ค่าอุณหภูมิวกฤต ค่าความดันวิกฤต และจุดเดือด นอกจากนี้วิธีของกานีและวิธีของเบนสันสามารถทำนายได้ใกล้เคียงกับค่าที่ใช้อ้างอิงสำหรับค่าพลังงานอิสระการก่อเกิดสารที่สภาวะมาตราฐาน และเมื่อได้นำเอาวิธีกรุ๊ปคอนทริบิวชันมาประยุกต์ใช้ในโปรแกรมจำลองแอสเพนพลัส วิธีกานีและวิธีเบนสันให้ค่าผลลัพธ์ที่ได้ใกล้เคียงกับค่าที่ได้จากการทดลอง แต่อย่างไรก็ตามวิธีของกานีนั้นไม่สามารถที่จะแยกความแตกต่างของคุณสมบัติของสารบางตัวออกจากกันได้ ผลการการศึกษาพบว่า 30 เปอร์เซ็นต์ของเอทานอลบริสุทธิ์สามารถถูกเติมลงไปเพื่อทำปฏิกิริยากับแก๊สโซลีนซึ่งทำให้ผลิตภัณฑ์ที่ได้ไม่เกินปริมาณสูงสุดของเอทานอล E10 อุณภูมิที่เหมาะสมในการทำปฏิกิริยาอีเทอริฟิเคชันสำหรับเอทานอลบริสุทธิ์คือ 70 องศาเซลเซียส

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KHAMRON YOOTHONGKHAM: THERMODYNAMIC STUDY OF ETHERIFICATION REACTIONS BETWEEN GASOLINE FROM FLUIDIZED CATALYTIC CRACKING AND ETHANOL. THESIS ADVISOR: ASSOC. PROF. SUTTICHAI ASSABUMRUNGRAT, Ph.D., THESIS COADVISOR: ASSIST. PROF. WORAPON KIATKITTIPONG, D.Eng, 148 pp.

This thesis investigates thermodynamic study of etherification reactions between gasoline from fluidized catalytic cracking and ethanol 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. Ambrose'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, 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. 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. The result found that 30 vol% of pure ethanol can be added to react with gasoline in order that the obtained product does not exceed the maximum allowable of ethanol in E10. The optimum etherification temperature for pure ethanol is 70 ° C.

Department ...Chemical Engineering.......	Student's signature ..คำรณ อยู่ทองคำ..
Field of Study ..Chemical Engineering.....	Advisor's signature ....
Academic year ....2007..............	Co-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]
MeOH	Methanol
EtOH	Ethyl alcohol
IPA	Isopropyl alcohol
BuOH	n-butanol
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
TEL	tetraethyl lead
VOCs	volatile organic compounds
2M1P	2-methyl-1-pentene
2M2P	2-methyl-2-pentene

2M2EXP	2-methyl-2-ethoxypentane
C3M2P	cis-3-methyl-2-pentene
T3M2P	trans-3-methyl-2-pentene
2E1B	2-ethyl-1butene
3M3EXP	3-methyl-3-ethxoypentane
23DM1B	2,3-dimethyl-1-butene
23DM2B	2, 3-dimethyl-2-butene
23DM2EXB	2,3-dimethyl-2-ethoxybutane
1MCYP	1-methylcyclopentene
1M1EXCYP	1-methyl-1-ethoxycyclopentane
2M1H	2-methyl-1-hexene
2M2H	2-methyl-2-hexene
2M2EXH	2-methyl-2-ethoxyhexane
C3M2H	cis-methyl-2-hexene
T3M2H	trans-3-methyl-2-hexene
C3M3H	cis-3-methyl-3-hexene
T3M3H	trans-3-methyl-3-hexene
2E1P	2-ethyl-1-pentene
3M3EXH	3-methyl-3-ethoxyhexane
23DM1P	2,3-dimethyl-1-pentene
23DM2P	2, 3-dimethyl-2-pentene
C34DM2P	cis-3,4-dimethyl-2-pentene
T34DM2P	trans-3,4-dimethyl-2-pentene
2E3M1B	2-ethyl-3-methyl-1-butene
23DM3EXP	2,3-dimethyl-3-ethoxypentane
24DM1P	2, 4-dimethyl-1-pentene
24DM2P	2,4-dimethyl-2-pentene
24DM2EXP	2,4-dimethyl-2-ethoxypentane
3E2P	3-ethyl-2-pentene
3E3EXP	3-ethoxy-3-ethoxypentane
233TM1B	2,3,3-trimethylbutene
233T2EXB	2,3,3-trimethyl-2-ethoxybutane
1ECYP	1-ethylcyclopentene

1E1EXCYP	1-ethyl-1-ethoxycyclopentane
12DMCYP	1,2-dimethylcyclopentene
15DMCYP	1, 5-dimethylcyclopentene
12D1EXCY	1, 2-dimethyl-1-ethoxycyclopentane
13DMCYP	1, 3-dimethylcyclopentene
14DMCYP	1, 4-dimethylcyclopentene
13D1EXCY	1,3-dimethyl-1-ethoxycyclopentane
1MCYH	1-methylcyclohexene
1M1EXCYH	1-methyl-1-ethoxycyclohexane

CHAPTER I

INTRODUCTION

Rational

The rapidly increase of gasoline demanding and environmental impact of gasoline. So, the federal had to restricted regulations environmental effect. In Gasoline, there are many compounds present in the exhaust of gasoline motor vehicles via both combustion and evaporation. It had many works to attempt improve gasoline fuel oil. Reformulated gasoline has been increased interest in recent year Oktar et al. (1999) several research of gasoline improvement is reported. Because of the reformulated gasoline is the fuel oil that improved the composition following with the environmental regulations i.e., olefin, aromatic and benzene content less than 18, 25 and 1 vol%, respectively, follow to Fan et al. (2004) and Zhao et al. (2007) hydroisomerization and aromatization a FCC gasoline upgrading process were reported by Fan et al.. The objective of this research is preserving the octane number and reduces olefin content in gasoline. Benzene is one of the key aromatic hydrocarbons desirable in gasoline for its high octane (~100). But the impact of gasoline on environments directly related to its fuel properties and contents such as octane number is one of gasoline properties but the compound that use to enhance are toxic, benzene is carcinogenic, olefins form engine fouling gums, smoke and smog. It is present in automotive evaporation and refueling vapors as well as in their exhausts. The positive octane impact has been offset by its tendency to induce severe health hazards as it is a known carcinogenic. Furthermore, olefins can also be removed by selective saturation and by isomerization processes. By this way, Zhao et al. (1999) had investigated the method to compensate the loss of gasoline octane number due to olefin reduction can be solved by the increased contents of isoparaffins and aromatics. Also, the alkylation reactions can be converted gasoline to high octane fuel oil. Alkylation is an excellent blending component for a high octane component free of lead, benzene and olefins. Another ways, oxygenate blending such as Methyl tertiary butyl ether (MTBE) and Tertiary amyl methyl ether (TAME) are main oxygenates compounds used in gasoline in addition to their high octane numbers. The oxygenated is the effective way to improve oxygen content and octane number. But oxygen is not a natural component of gasoline. It is added in the form of "oxygenates," which are organic combustible liquids which have an oxygen atom in their structure. An oxygenate can be added to fuel oil that can reduce pollution and improve of combustion efficiency, like, reducing CO content and hydrocarbon emission from exhaust pipe. Each oxygenate contains a different amount of oxygen on a weight percentage basis, so different volumes of the different oxygenates are required to achieve the required oxygen content. Reformulated gasoline is required to contain an average of 2.1 wt%. The vapor pressure will be solved with enhance the gasoline octane number by etherification CDTECH et al. (2004). TAME can be produce from C5 olefin and methanol and be used octane enhancer. At present, two different classes of oxygenates are being added to gasoline: alcohols and ethers. Ethanol is the alcohol most commonly added to gasoline. Since it is a renewable energy, CO_2 produced from ethanol combustion is not considered as a global warming contributor. However, most of present car can be run on gasoline restrictedly blended with some ethanol content, i.e. 10-20 vol%. Furthermore, alcohols can be made the lower NOx emission; hence, alcohols had been used 100% purity so the sulfur problem and NOx emission can be reduced. But, the aldehyde emissions have been observed to increase when the alcohols had been used for automobiles. In addition to, the potential vapor problem may arise with the alcohols in unventilated areas. Therefore the chance of using ethanol as a fuel extender is limited. Furthermore, many recent researches reported disadvantages of the gasohol. With a present standard of engine and the use of catalytic converter, the emissions at the end pipe are relatively small while evaporative emissions have become significant. Evaporative emissions are considered as a loss of fuel which can be occurred from diurnal, running loss, hot soak and refueling.

Ethanol derived ethers can overcome the drawback of gasoline with direct ethanol blend. Ethers/gasoline fuel shows less volatility than gasohol. Oxygenated is substances that the molecular that content of oxygen in chain. Oxygenates may be based on alcohols or ethers. The most common oxygenates in use are: Alcohol such as Methanol (MeOH), Ethanol (EtOH), Isopropyl alcohol (IPA), n-butanol (BuOH). Ethers: such as Methyl tert-butyl ether (MTBE), Tertiary amyl methyl ether (TAME), Tertiary hexyl methyl ether (THEE), Ethyl tertiary butyl ether (ETBE), Tertiary amyl ethyl ether (TAEE), Diisopropyl ether (DIPE). Oxygenates are usually employed as gasoline additives to reduce carbon monoxide that is created during the burning of the fuel. Some oxygenates such as MTBE have been found to have contaminated groundwater, mostly through leaks in underground gasoline storage tanks. In 2004, California and New York banned MTBE, generally replacing it with ethanol. Several other states started switching soon afterward.

The fluidized bed catalytic cracking unit (FCC) may be has gasoline containing total olefins of about 50 to 65 vol% with their reactive olefins of 55 to 60 vol% is potential valuable feedstock for production of oxygenate ethers Pescarollo et al. (1993). The success of the process was reported by Piyaporn et al. (2006), who etherified FCC light gasoline with ethanol. The improvements in octane number and volume by reducing olefin and bRvp of the gasoline were reported. However, such a kind of thermodynamic investigation has not yet been carried out. Because of the group contribution method can be solve for engineer problem, it is used to estimate the properties that not appear in data handbook. This estimation method allowed calculating the missing properties by molecular structure. There are several of group contribution method such as Joback's method, Gani's method, Yoneda's method and Benson's method etc. When the molecular structures begin to complex then the method that included considered more are applied. Many hydrocarbons are usually lack of data about critical temperature, critical pressure and Gibbs free energy of formations. The objectives of the study were to study the thermodynamic equilibrium for etherification of FCC gasoline and ethanol by using a simulation program. Therefore, the aim of this research is the evaluation of thermodynamic limits of the process considered in which a very large number of components is involved. The objective of this research that to study the thermodynamic equilibrium for etherification of FCC gasoline and ethanol by using a simulation program and estimate the properties using group contribution method.

CHAPTER II

THEORY

This chapter will be described the detail of FCC light gasoline as the product from FCC unit. FCC light gasoline have been containing of reactive olefins. The reactive olefin can be reacting with ethanol to get alkyl ether. Both ethanol and ether can be enhancer of fuel oil properties such as octane number and vapor pressure. Aspen plus program is applied to study equilibrium of reactive olefins with ethanol. Aspen plus is the program as flexibility, power full for process engineer and easy to use. The engineers can be facing with the lack of data such as critical properties, thermodynamic properties. The group contribution method is applied to calculate the properties. The various group contribution methods will be used such as Ambrose, Joback, Gani and Benson. The catalyst that suitable for etherification should be acid catalyst such as Amberlyst 15, Amberlyst 16 and zeolite.

2.1 Fluidize Catalytic Cracking gasoline

2.1.1 FCC unit

Fluidize catalytic cracking (FCC), 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 catalytic cracker, Due to the high demand for gasoline. The process was first used in around 1942, and employs a powdered catalyst. FCC unit has the advantage that gasoline of high quality can be produced from almost any crude oil in equipment subject to careful control and operated at a low pressure, hence at comparatively lower cost. Moreover, as shown by the typical analysis in Table 2.1, the yields of light cuts obtained on a fluid bed catalytic cracking installation, for instance, optimimized for the maximum production of middle distillates constitutes a large fraction of the feedstock (15 to 20 percent weight). 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. The catalyst is usually obtained by crushing pumice stones, which contain mainly aluminium oxide and silicon(IV) oxide into small, porous pieces. 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 olefin profile. Olefins in gasoline are responsible for the formation of polymeric deposits in storage tanks, fuel ducts and injectors.

2.1.2 FCC light gasoline

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).

Table 2.1 Fluidized bed catalytic cracking adjusted for maximum production of middle distillates typical yield (Chauvel, A. & Lefebvre, G., 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

The effluent gasoline from the FCC unit has the reactive olefins that can be etherified with ethanol to produce the ethers. The reactive olefins present in FCC gasoline and their corresponding ethers formed by ethanol addition are shown as follows;

Reactive olefins	**B.P., °C**	**Ethylic ethers**
C4		
Isobutene	-6.3	2-methyl-2-ethoxy propane (ETBE)
C5		

2-methyl-2-butene	31.1	2-methyl-2-ethoxy butane (TAEE)
2-methyl-l-butene	38.6	2-methyl-2-ethoxy butane (TAEE)
C6		
2-methyl-l-pentene	62.0	2-methyl-2-ethoxy pentane
2-methyl-2-pentene	67.3	2-methyl-2-ethoxy pentane
Cis-3-methyl-2-pentene	67.7	3-methyl-3-ethoxy pentane
Trans-3-methyl-2-pentene	70.4	3-methyl-3-ethoxy pentane
2-ethyl-l-butene	64.7	3-methyl-3-ethoxy pentane
2, 3-dimethyl-l-butene	53.6	2, 3-dimethyl-2-etoxy butane
2, 3-dimethyl-2-butene	73.2	2, 3-dimethyl-2-etoxy butane
l-methylcyclopentene	75.5	l-methyl-l-ethoxy cyclopentane
C7		
2-methyl-l-hexene	92.0	2-methyl-2-ethoxy hexane
2-methyl-2-hexene	95.2	2-methyl-2-ethoxy hexane
Cis-3-methyl-2-hexene	97.3	3-methyl-3-ethoxy hexane
Trans-3-methyl-2-hexene	95.2	3-methyl-3-ethoxy hexane
Cis-3-methyl-3-hexene	95.4	3-methyl-3-ethoxy hexane
Trans-3-methyl-3-hexene	93.5	3-methyl-3-ethoxy hexane
2-ethyl-l-pentene	94.0	2-ethyl-2-ethoxy pentane
2, 3-dimethyl-l-pentene	84.2	2, 3-dimethyl-2-ethoxy pentane
2, 3-dimethyl-2-pentene	97.4	2, 3-dimethyl-2-ethoxy pentane
Cis-3,4-dimethyl-2-pentene	89.2	2,3-dimethyl-3-ethoxy pentane
trans-3,4-dimethyl-2-pentene	91.5	2,3-dimethyl-3-ethoxy pentane
2-ethyl-3-methyl-l-butene	86.3	2, 3-dimethyl-3-ethoxy pentane
2, 4-dimethyl-l-pentene	81.6	2, 4-dimethyl-2-ethoxy pentane
2, 4-dimethyl-2-pentene	83.3	2, 4-dimethyl-2-ethoxy pentane
3-ethyl-2-pentene	96.0	3-ethyl-3-ethoxy pentane
2, 3, 3-trimethyl-l-butene	77.6	2, 3,3-trimethyl-2-ethoxy butane
l-ethylcyclopentene	106.3	l-ethyl-l-ethoxy cyclopentane
1,2-dimethylcyclopentene	106.8	1,2-dimethyl-l-ethoxy cyclopentane
1,5-dimethylcyclopentene	102.0	1,2-dimethyl-l-ethoxy cyclopentane
1,3-dimethylcyclopentene	92.0	1,3-dimethyl-l-ethoxy cyclopentane
1,4-dimethylcyclopentene	93.2	1,3-dimethyl-l-ethoxy cyclopentane

l-methylcyclohexene	110.0	l-methyl-l-ethoxy cyclohexane

* Boiling point available from Pescarollo (1995).

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 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. For volatile petroleum products, vapor pressure is used as an indirect measure of evaporation rate. The 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).

2.2.2 Octane Number

Octane number represents the resistance of gasoline to premature detonation when exposed to heat and pressure in the combustion chamber of an internal-combustion engine. The octane number of fuel is determined by burning the gasoline in an engine under controlled conditions, e.g., spark timing, compression, engine speed, and load, until a standard level of knock occurs. Octane is measured relative to a mixture of isooctane (2, 2, 4-trimethylpentane, an isomer of octane) and n-heptane which octane number are 100 and 0, respectively. At present three systems of octane rating are used in the United States. Two of these, the research octane number (RON) and motor octane numbers (MON), are determined by burning the gasoline in an engine under different, but specified, conditions. Usually the MON is lower than the RON. The third octane rating, which federal regulations require on commercial gasoline pumps, is an average of research octane and motor octane. The regular grade gasoline has an octane number of about 87 and a premium grade of about 93.

2.2.3 Distillation Temperature

Gasoline is a mixture of many different compounds, each having its own boiling point and vapor-forming characteristics. 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. Gasoline 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 small 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.

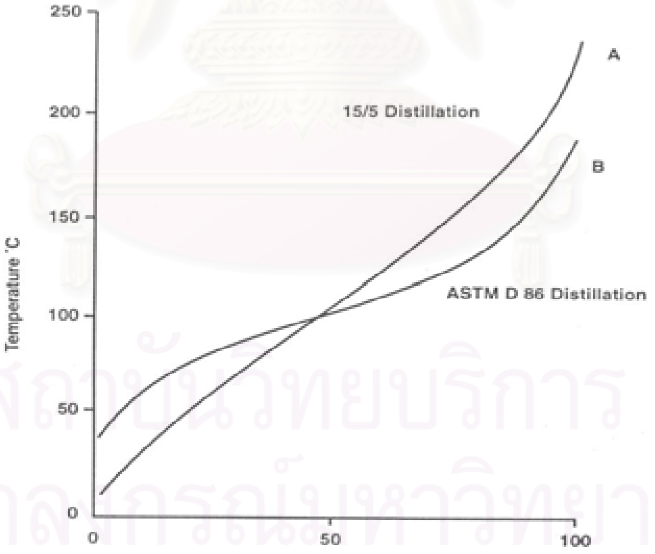


Figure 2.1 Gasoline distillation curve (Owen and Coley, 1995)

2.3 Oxygenated fuel

The oxygenate fuel can be divided by 2 type, alcohol and ether. Both of these had been used to fuel oil enhancer. The addition of oxygenate can improve both combustion and octane number.

2.3.1 Alcohol

Recently, considerable attention has been given to alcohol fuel production from biomass. A specific application is the possibility of blending biomass-derived alcohol with gasoline to produce a transportation fuel. It is technologically possible to develop a liquid transportation fuel system based on alcohol-gasohol blends. To use of alcohol-based fuels is not a new concept. In fact, alcohols have been utilized extensively throughout the world as petroleum substitutes during periods of shortage. The relative abundance and low cost of petroleum since the end of World War II reduced the importance of alcohol fuels. Today's petroleum shortages have created the importance of alcohol fuels. This has stimulated new research into applications and bioconversion techniques, as well as reassessment of the environmental advantages/disadvantages of using alcohol fuels.

More than 80% of the total waste disposal costs can be attributed to collection; consequently, for many seasonal wastes it is not economical to collect and dispose of them. This is also the reason why urban wastes are routinely disposed of near their collection sites. Crop residues represent more than 44% of the total estimated residue in the U.S. More than 95% of the field crops planted are for food grains. The majority of the residuals (e.g., corn stalks, wheat straw, etc.), are left unused and to decompose once the crop has been harvested. More than 350 tonnes of dry organic residue are generated annually (Table 2.2). The amount of waste generated from urban areas is generally a function of population size. Larger cities to tend, however, to generate more commercial refuse per capita than smaller cities. Urban wastes vary greatly in composition. In general, roughly 50% of the bulk weight tends to be inorganic matter and water. The remaining portion represents dry organic material having a potential energy value. Among industrial waste, the lumber and food processing industries are the largest contributors of organic matter suitable for energy production. The chemical and manufacturing industries on the whole generate low amounts of organic matter. Food processing wastes vary greatly in both composition and moisture content.

Roughly 30% or more of these residues are use in byproducts. The remaining wastes, which are disposed of, generally have low heating value in the range of 11,600-18,600 J/kg. Alcohols as a fuel offer promising alternatives to fossil-based liquid fuels. Various biomass fuel production routes and biomass feedstock are illustrated in Figure 2.2. Methanol and ethanol are considered to be the most promising alcohols, suitable for extensive use as transportation fuels. However, as will be discussed in subsequent chapters, a variety of other alcohols and energy related applications can be derived from biomass. In Table 2.2, the crop residues and manures constitute the major sources of organic wastes. Of all the materials listed, only urban refuse is collected routinely. Crop and logging residues are collected seasonally but not on an organize basis.

Table 2.2 Estimated solid wastes for biomass feedstock in U.S. [Nicholas et al. 2004]

	Estimated wastes		total	water
	(106 tones/yr)		waste	content
Biomass source	dry basis	wet basis	%	%
Urban refuse	117.9	235.9	14.7	66.7
Crop residues	353.8	499.0	44.3	58.5
Manures	181.4	1361-1814	22.7	88-91
Industrial wastes	39.9	99.8	5.0	71.4
Logging wastes	49.9	72.6	6.2	59.3
Sewage	10.9	-	1.4	-
Miscellaneous	45.4	-	5.7	-
Total waste	799.2	2268-2722	100	74-78

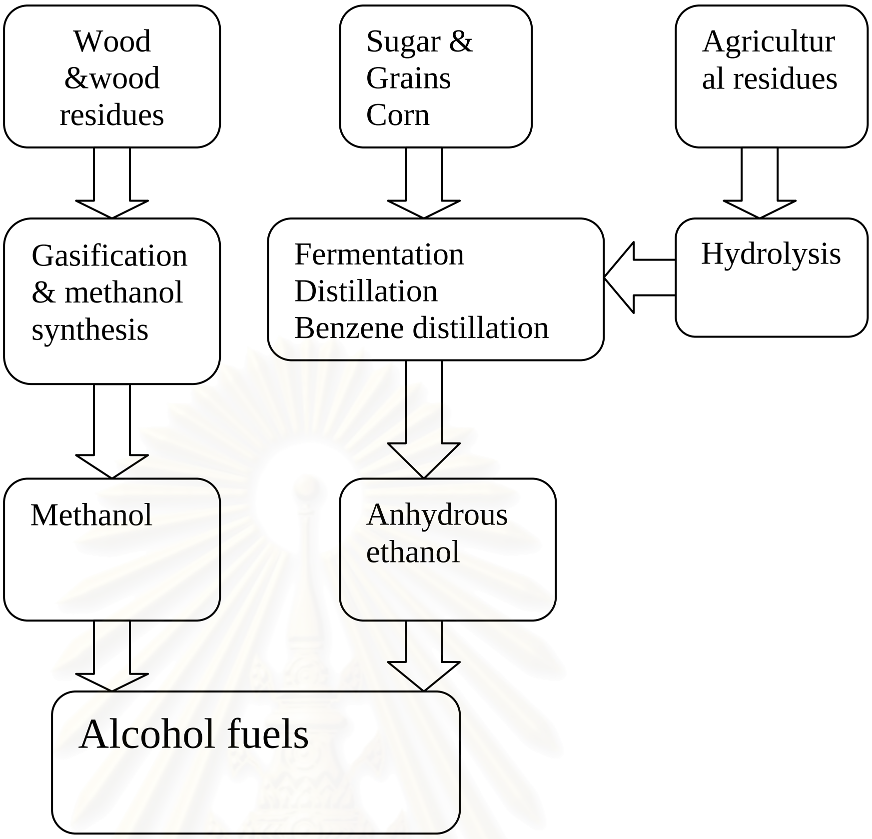


Figure 2.2 Scheme of the general approaches to the production of Ethanol and methanol.

2.3.2 Ethers

Ether is a class of chemical compounds which contain an ether group — an oxygen atom connected to two (substituted) alkyl or aryl groups — of general formula **R–O–R'**. The example for etherification reaction of isobutene with ethanol is showed in Figure 2.3.

Ether molecules cannot form hydrogen bonds among each other, resulting in a relatively low boiling point comparable to that of the analogous alcohols. However, the differences in the boiling points of the ethers and their isometric alcohols become smaller as the carbon chains become longer, as the hydrophobic nature of the carbon chain becomes more predominant over the presence of hydrogen bonding.

Ethers are slightly polarity as the C - O - C bond angle in the functional group is about 110 degrees, and the C - O dipole does not cancel out. Ethers are more polar than alkenes but not as polar as alcohols. The using of the first tertiary ether, methyl tert-butyl ether (MTBE) as oxygenate was first used in commercial gasoline in Italy in 1973 and in the US by ARCO in 1979. Ethers can be derived from fossil fuels such as MTBE and TAME, or partly from biomass such as ETBE and TAEE.

2.3.2.1 MTBE

It is obtained through the reaction of isobutene and methanol. The use of MTBE has grown tremendously since it was introduced in 1973.Recently MTBE has gained considerable negative publicity. After it was detected in ground water in California, the state government passed legislation that prohibits its use in California by the end of the year 2002. Unlike other gasoline components, MTBE is highly soluble in water. With a solubility of 4.3 wt%, it is tens of times more water-soluble than any non-oxygenate component of gasoline. Once it gets into the ground, MTBE travels through the soil into ground water, where it is easily detected even at very low concentrations owing to its distinctive taste and odor. Leaking storage tanks were the main source of the MTBE in soil and ground water in California. The situation is better in Europe because double-walled storage tanks are common. MTBE degrades in sunlight, but very slowly in soil or ground water. As MTBE is a relatively new component in the ecosystem, microorganisms have not yet developed the capability to break it down. The US Environmental Protection Agency, EPA, has examined MTBE as a potential carcinogen, but recently it was decided that MTBE should not be classified as a human carcinogen. The health effects of MTBE continue to be somewhat obscure. However, we must bear in mind that some other components of gasoline have been proven far more toxic than MTBE is even suspected of being. For example, MTBE has replaced lead components and, in part, benzene, both of which are known to be toxic and hazardous for human health.

2.3.2.2 TAME

It is obtained by reacting methanol with two of C_5 iso-olefins, 2-methyl-2-butene, 2M2B, and 2-methyl-1-butene, 2M1B. The third C_5 iso-olefin, 3-methyl-1-butene is completely inert toward the reaction with methanol. The TAME potential capacity is strictly related to the reactive isoamylene present in the light gasoline catalytic cracking plants, An additional minor contribution to TAME capacity can arise from C_5 coming from naphtha steam cracking for ethylene manufacture, after a selective hydrogenation to remove dienes. Although TAME may solver the problem of water contaminant over MTBE as its significant lower in water solubility. It still derived from methanol which currently still derived from natural gas as mention earlier.

2.3.2.3 ETBE and TAEE

The ethyl ether, ETBE and TAEE are produced by the addition of ethanol to isobutene and reactive isoamylene, respectively. Ethyl ethers show similarly blending octane properties that methyl ethers while lower in bRvp and water solubility which are more favorable. Presently, TAEE is not in the market, while ETBE is produced in several countries (US and Europe), mainly in retrofit MTBE units, with similar yields and selectivity. Ethyl tert-butyl ether (ETBE) is commonly used as an oxygenate gasoline additive in the production of gasoline from crude oil. ETBE offers equal or greater air quality benefits as ethanol, while being technically and logistically less challenging. Unlike ethanol, ETBE does not induce evaporation of gasoline, which is one of the causes of smog, and does not absorb moisture from the atmosphere. It is synthesized by mixing ethanol and isobutylene and react them with heat over a catalyst.

Figure 2.3. Scheme of isobutylene reaction

Ethanol, produced by fermentation and distillation, is more expensive than methanol, which is derived from natural gas. Therefore, MTBE, made from methanol is cheaper than ETBE, made from ethanol. However, bio-ethanol makes ETBE partially a biofuel, while MTBE is entirely a fossil fuel and introduces a risk to the environment

Tertiary Amyl Ethyl Ether (TAEE) is formed by the catalytic etherification of isoamylene with ethanol. The process can be including to the use of an acidic ion exchange resin catalyst in fixed bed reactor or catalytic distillations. In this reaction, the conversion was limited by equilibrium. Finally, if the process can be exceeded equilibrium limitations, it would have been got the high conversion. It can be got the higher conversion of isoamylene.

2.4 Other Relating chemical reactions

2.4.1 Hydration reaction

Olefins can be reacted with water at the suitable of condition. Many alcohols had been used to octane enhancer. To eliminate lead-gasoline containing, the etherification to produce ether and hydration to produce alcohol are developed. The hydration reaction can be occurred in acidic catalytic reaction follow to Figure 2.4. The conventional acidic catalyst for hydration reaction is Amberlyst 15. Furthermore, the most common alcohol from hydration of olefins is isopropyl alcohol, tert-butyl alcohol and ethanol. In haft of its production of alcohol, the alcohol had been use to direct solvent. In addition to, the various applications including surface coatings, inks, pesticides formulation, electronics applications, chemical intermediates, pharmaceutical solvents, surface coatings, adhesives, lubricant oil dewaxing, magnetic tape and printing ink. In this research had been assume that only reactive olefins in FCC gasoline can be react with water. The possible alcohols are similar to ether. In addition to, the hydroxyl group will be substituted at the position of ethyl alcohol on alkyl ether follow to Figure 2.5.

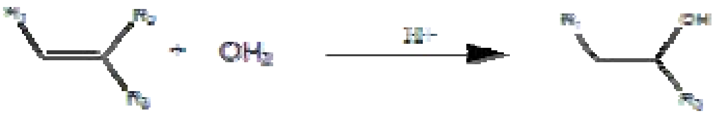


Figure 2.4 Hydration reactions of olefins with water

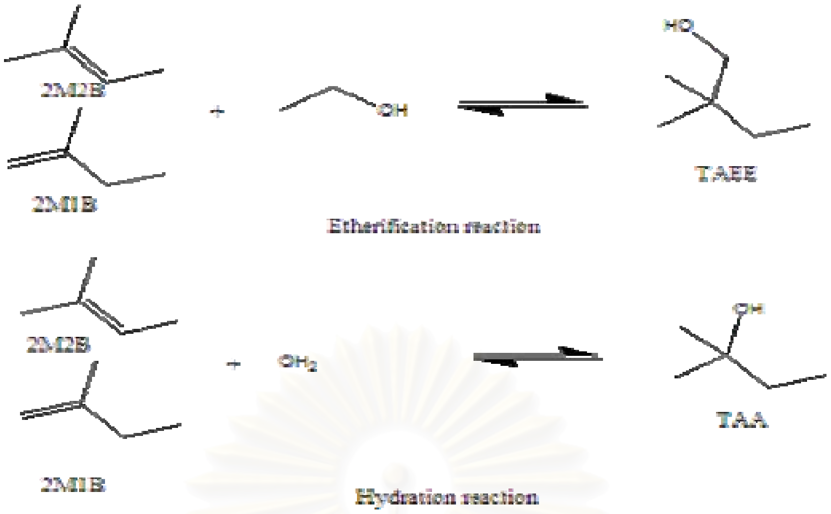


Figure 2.5 Etherification and hydration reaction of C5 olefins

2.4.2 Isomerization reaction

Isomers are several compounds with the same chemical formula. Stereoisomers are any pair of isomers that have the same connectivity. The molecules then need to be examined closely to see if the molecules are identical after rotation around single bonds. If the molecules are identical after rotation around single bonds then they are said to be conformers or conformational isomers or rotamers. Molecules with the same chemical formula, the same connectivity and which are not identical after rotation around single bonds are configurational isomers. There are several types of configurational isomer: enantiomers, diastereomers/epimers and geometric isomers (isomer showed in Figure. 2.6).

Isomerization reactions are showed follow to Figure 2.7. In this research had been assume that the isomerization will be occurred at α-olefins and β-olefins of reactive olefins. The example for isomerization reaction of reactive olefins 2M1B ⇔2M2B, 2, 3-Dimethyl-1-Butene ⇔ 2, 3-Dimethyl-2, Butene etc,. The

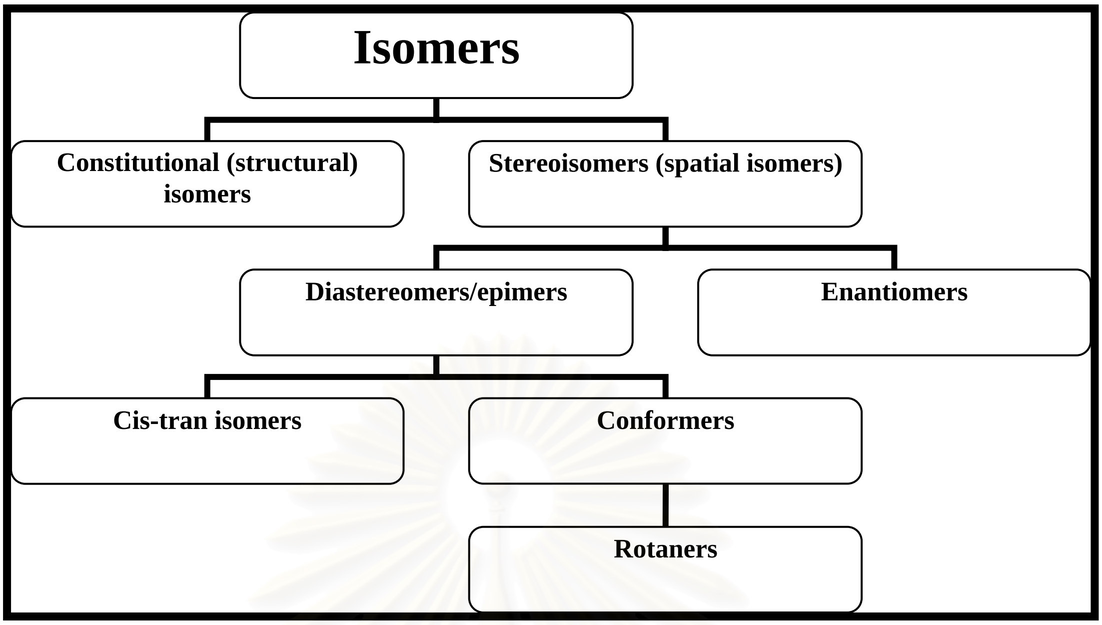


Figure 2.6 The scheme of isomer classification

Figure 2.7 Isomerization reactions of olefins

2.5 Group contribution method

In several situations, the project of engineer can face with the problem of experimental data of needed property is not available. The value can be estimated or predicted. Estimates may be based on theory, on correlations of experimental data or combining of both. In the system for estimation property would provide reliable physical and thermodynamic properties for pure substances and for mixture at any temperature, pressure and composition. One of the first successful group contribution methods to estimate critical properties was developed by Lydersen et al. (1995). Since, more experimental data were reported. Estimation technique was continuously developed.

2.5.1 Ambrose's method Ambrose's method is reported by Ambrose that is available in a National Physical Laboratory. In this method, the three critical properties T_c, P_c, and V_c are estimated by a group contribution technique using the following relations:

$$T_c = T_b[1 + (1.242 + \sum \Delta_T)^{-1}] \tag{2.1}$$

$$Pc = M(0.339 + \sum \Delta_p)^{-2} \tag{2.2}$$

The units employed are Kelvin and bars. The Δ quantities are evaluated by summing contributions for various atoms or groups of atoms. To employ these relations, the normal boiling point T_b (at 1 atm) and the molecular weight M are needed. The functional groups from Ambrose's group contribution are listed in Appendix A.

2.5.2 Joback's method

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

$$T_c(K) = T_b[0.584 + 0.965\{\sum_k N_k(tck)\} - \{\sum_k N_k(tck)\}^2]^{-1} \tag{2.3}$$

$$P_c(bar) = [0.113 + 0.0032N_{atoms} - \sum_k N_k(pck)]^{-2} \tag{2.4}$$

$$T_b = 198 + \sum_k N_k(tbk) \tag{2.5}$$

$$\Delta G_f^0 = 53.88 + \sum_k N_k(gfk) \tag{2.6}$$

where 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 B. For calculation of Tc, the value of the normal boiling point, Tb, is needed.

2.5.3 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 group located close together, resonance structures, etc., at the “first order”. The general CG formulation of a function f [F] of a property F is

$$F = f[\sum_k N_k (F_{1i}) + W \sum_j M_j (F_{2j})] \qquad (2.7)$$

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;

$$Tc(K) = 181.128 \ln[\sum_k N_k (tc1k) + W \sum_j M_j (tc2j)] \qquad (2.8)$$

$$Pc(bar) = [\sum_k N_k (pc1k) + W \sum_j M_j (pc2j) + 0.10022]^{-2} + 1.3705 \qquad (2.9)$$

$$Tb(K) = 204.359 \ln[\sum_k N_k (tb1k) + W \sum_j M_j (tb2j)] \qquad (2.10)$$

$$\Delta G_f^o (kJmol^{-1}) = -14.83 + [\sum_k N_k (gf1k) + W \sum_j M_j (gf2j)] \qquad (2.11)$$

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 C.

2.5.4 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;

$$\Delta H_f^o(298.15K) = \sum_k N_k(\Delta H_{fk}^o) \tag{2.12}$$

$$S^o(298.15K) = \sum_k N_k(S_k^o + S_s^o) + S_s^o \tag{2.13}$$

$$S_{el}^o(298.15K) = \sum_e v_e(S_e^o) \tag{2.14}$$

$$\Delta G_f^o(298.15K) = \Delta H_f^o(298.15K) - 298.15[S^o(298.15K) - S_{el}^o(298.15K)] \tag{2.15}$$

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

$$S_s^o = R\ln(N_{oi}) - R\ln(N_{ts}) \tag{2.16}$$

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 (2.16). The two cases can be nonunit 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;

$$N_{ts} = N_{es} \bullet \prod_{k=term} (N_{is})_k \tag{2.17}$$

2.5.5 Unifac method

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:

$$g = g^C + g^R \qquad (2.18)$$

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,

$$g^C = \sum x_i \ln \frac{\phi_i}{x_i} + 5 \sum q_i x_i \ln \frac{\theta_i}{\phi_i} \qquad (2.19)$$

and

$$g^R = -\sum q_i x_i \ln(\sum \theta_j \tau_{ji}) \qquad (2.20)$$

where

$$\phi_i = \frac{x_i r_i}{x_j r_{j\ i}} \tag{2.21}$$

and

$$\theta_i = \frac{x_i q_i}{x_j q_{j\ i}} \tag{2.22}$$

Subscript i identify 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. (2.21), which are temperature dependent:

$$\tau_{ji} = \exp\frac{-(u_{ji} - u_{ii})}{RT} \tag{2.23}$$

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. (2.19) to (2.21)]. The result is given by the following equations:

$$\ln\gamma_i = \ln\gamma_i^{C} + \ln\gamma_i^{R} \tag{2.24}$$

$$\ln\gamma_i^{C} = 1 - J_i + \ln J_i - 5q_i(1 - \frac{J_i}{L_i} + \ln\frac{J_i}{L_i}) \tag{2.25}$$

and

$$\ln \gamma_i{}^R = q_i(1 - \ln s_i - \sum \theta_j \frac{\tau_{ij}}{s_j}) \tag{2.26}$$

where in addition to Eqs (2.23) and (2.24)

$$J_i = \frac{r_i}{\sum x_j r_j} S \tag{2.27}$$

$$L_i = \frac{q_i}{\sum x_j q_j} S \tag{2.28}$$

$$s_i = \sum \theta_l \tau_{li} \tag{2.29}$$

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:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \tag{2.30}$$

when

$$\ln \gamma_i^C = 1 - J_i + \ln J_i - 5q_i(1 - \frac{J_i}{L_i} + \ln \frac{J_i}{L_i}) \tag{2.31}$$

and

$$\ln \gamma_i^R = q_i[1 - (\theta_k \frac{\beta_{ik}}{s_k} - e_{ki} \ln \frac{\beta_{ik}}{s_k})] \tag{2.32}$$

The quantities J_i and L_i are given by:

$$J_i = \frac{r_i}{x_j r_j} \tag{2.33}$$

$$L_i = \frac{q_i}{x_j q_j} \tag{2.34}$$

In addition to, the following definition of parameters in Eqs. 2.31 and 2.32 apply:

$$r_i = v_k^{(i)} R_k \tag{2.35}$$

$$q_i = v_k^{(i)} Q_k \tag{2.36}$$

$$e_{ki} = \frac{v_k^{(i)} Q_k}{q_i} \tag{2.37}$$

$$\beta_{ik} = e_{mi} \tau_{mk} \tag{2.38}$$

$$\theta_{ik} = \frac{x_i q_i e_{ki}}{x_j q_j} \tag{2.39}$$

$$s_k = \theta_m \tau_{mk} \tag{2.40}$$

$$\tau_{mk} = \exp(\frac{-a_{mk}}{T}) \tag{2.41}$$

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.

2.6 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.

2.6.1 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.

2.6.2 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.

2.7 Catalyst

2.7.1 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 2.8) and with electrically charged sites at which one ion may replace another in a process called ion exchanging.

Figure 2.8 Ion exchange resin beads

2.7.2 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 to, 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 crosslink which depends on the % cross linkage 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 cross linking 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 -SO3H which is strongly ionized to -SO3

2. Strongly basic; -NR3+ 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. Weakly basic; -NH2 that weakly attracts protons to form NH3+, -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.

2.7.3 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.

2.7.4 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 cross linkage 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 cross linked, the more difficult to introduce additional functional groups. Sulfonation is carried out after the cross linking 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 cross linked 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 cross linked resin, these groups are spaced closer together on a volume basis because the volume of water is reduced by the additional cross linking. 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. Cross linkage has a definite influence on the time required for an ion to reach equilibrium. An ion exchange resin that is highly cross linked 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 cross linked the polymer, the longer the time is required to reach equilibrium conditions.

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.

Table 2.3 Diameter of particles related to mesh range

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 ion 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.

CHAPTER III

LITERATURE REVIEWS

This chapter contains the research reviews of etherification of reactive olefins and alcohol in both experiment and simulation. The reaction that possible to be occurred is hydration, isomerization and etherification. Both of thermodynamics and kinetics studies have been reviewed.

3.1 Etherification reactions

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. These oxygenates can be produced from the etherification of olefin compounds with alcohol such as methanol and ethanol over a protonated cation exchange resin catalyst such as Amberlyst 15 and Amberlyst 16 or acidic zeolite.

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 obtained with H-Beta zeolite as well as Amberlyst 15 with in 12 h. Zeolite H-Beta zeolite 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. Methyl tert-butyl ether (MTBE) had act to important additive compound for a while, however, it dissolve to underground water so the higher molecular of ether was substituted to add to fuel oil.

TAME can be synthesized by the etherification of isoamylene (IA) with methanol with ion-exchange resin bead catalysts such as; Amberlyst 16 (Rihko et al., 1994; Paakkonen et al., 2003; Wang et al., 2002) had studied in Si-MCM41 supported Zirconia and Nafion by using Amberlyst 15 as a reference catalyst for the etherification of C6 olefins with methanol Si-MCM41 supported Zirconia and Nafion catalyst produced higher selectivity than Amberlyst 15 while lower conversion. Rihko & Krause (1993) published the report for the reactivity of IA with EtOH. It was found that 2M1B was more reactive than 2M2B which is good in agreement with other researches (Rihko et al. 1994); Oktar et al. (1999) study the etherification of C_5 reactive olefins (2-methyl-1-butene and 2-methyl-2-butene) with ethanol catalyzed by Amberlyst 15 are investigated in 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. The equilibrium of TAEE synthesis reaction has been studied by Rihko et al. (1994). Likewise, Kitchaiya et al. (1996) provided a thermodynamic analysis for equilibrium of simultaneous IA etherification and isomerization reaction. It was found that the observation equilibrium constant corresponded with the thermodynamic value.

Subsequently, Linnekoski et al. (1999) studied the simultaneous etherification and hydration reaction of IA. They also focused on the effect water adsorption on TAEE formation by using an azeotropic mixture of ethanol and water as reagent. The Langmuir-Hishelwood-Hougen-Watson (LHHW) model as was employed a proposed kinetic model. It was observed that water is an essential inhibitor for TAEE formation. A slight amount of water can largely retard the IA conversion.

However, all above literature are based on C4 and C5 olefins. The supply of olefinic i.e., IB and IA are unlikely to meet demand for etherification feeds. Heavier reactive olefins should be considered as additional feeds for ether production.

Zhang et al. (1995) had studied the kinetics of isomerization and etherification of C6 olefins with ethanol catalyzed be Amberlyst 15 to produce 3-methyl-3-ethoxy-pentane (THEE). The kinetic rate expressions are based on the Langmuir-Hishelwood-Hougen-Watson 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. In addition, the term of olefins and ether adsorption can be neglected but the vacant sites can not be neglected. 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.

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.

However, methanol and methanol derivatives such as MTBE and TAME are not favorable in an environment view point because they are still mostly derived from natural gas whose production may contribute to global warning. Methanol from renewable source has higher cost than from petroleum at the present. Therefore ethanol is now using for solving the global climate change and oil crisis. Since it is a renewable energy, the CO_2 produced from ethanol combustion is not considered as a global warming contributor because it is a part of the carbon cycle and therefore is carbon neutral.

Thipsunet et al. (2006) 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.

3.2 Olefins hydration

The several of alcohol such as tert-butyl alcohol, tert-amyl alcohol are produced from hydration between water and reactive olefins, i.e., IB and IA, respectively. Certain oxygenated organic compound had been known to be potentially suitable for use as fuels for combustion. The alcohols are proposed in admixture with hydrocarbon fuel. To improve the octane number of fuel oil, the many research had been revealed about the reaction of olefins and water. Linnekoski et al. (1998) studied the etherification and hydration between 95 % ethanol and C5 olefins. The conversion of C5 decreased with the water presence in the feed. Delik et al. (2003) studied the reaction in a batch reactive distillation column. The simultaneous productions of tert-amyl ethyl ether are investigated. The three components in system are isoamylene-ethanol-water which water showed the higher conversion than isoamylene. Because of the higher absorption of water at active site than isoamylene. Finally, the production of tert-amyl alcohol showed higher than the production of tert-amyl ethyl ether. Aiouache and Goto (2003) revealed the kinetic models of etherification of tert-amyl alcohol and ethanol. The Langmuir-Hishelwood-Hougen-Watson (LHHW) showed the slightly better than power law model. Fidel et al. (1993) had been study the effect of water presence in ethanol azeotropic mixture for ETBE and TAEE production. The result showed that with this amount of water presence in feed decreased the rate of ether production about 50%. However, the equilibrium conversions were not affected. The water can be totally consumed to produce tert-butyl alcohol and tert-amyl alcohol. The author concluded that the reaction between azeotropic mixture of alcohol and olefins can be successes in the process that has the length of reactor long enough to get the higher olefin conversion. Paakkonen et al. (2003) investigated the dehydration of the alcohol during the etherification of isoamylenes with methanol or ethanol. The result showed that the formation of dimethyl ether and diethyl ether are favored by increasing the operating temperature. The formation of DME was higher than that of DEE at high temperature. The model of absorption of component showed similar to Zhang et al. (1995) and Cunill et al. (1993) that the alcohol molecule absorbed and other molecule reacts from the liquid phase. Martin et al. (1993) disclosed the process for the production of a hydration product from an olefinic feedstock. This patent had been applied the several catalyst ZSM-22, ZSM-23, NU-10, ferriefite and theta-1 for alcohol production. In 1984 Robert et al. (1986) had been reported the process for coproduction of isopropanol and tert-butyl alcohol. This process had been applied to the dehydrogenation process which converts the paraffin to olefin. The rich olefin stream was contacted with water to produce C3-C4 alcohol. The fractionation was used to separate the alcohol products. Mohsen et al. (1989) had reported the integrated process of etherification and hydration. The iso-olefin feedstock is used to produce alkyl ether. The alcohols are extracted from the product so-called by-product. The alcohol by-product from this process is isopropanol, 1-butanol, 2-butanol and the like. In 1993 Mohsen et al. (1993) reported the catalyst for hydration of olefin process. The zeolite catalyst in FCC process will be withdrawn from process. And then catalyst will be mixed with fresh catalyst then was sent to hydration zone. The FCC stream that had rich C4+ olefins will be contacted with water to produced the alcohol. Due to alcohols have potential in solvent, intermediate and can be admixed to fuel oil. So, olefin feed stocks were potential source to produce both alcohol and ether.

3.3 Isomerization reaction

The objective of the isomerization reaction is to improve the octane rating of straight run gasoline n-paraffins isomerized to branched isoparaffins. The process must be specified with high yields and high selectivity to high octane isomeric forms. Miller et al. (2001) reported the condition for isomerization range of temperate 50 – 450 ^{o} C, but it favored of 100 ^{o} C. They studied the isomerization of normal C4 and C5 olefins convert to C5 reactive olefins of branch isomers. The conversion are greater than 50 wt% when use the porous matrix material catalyst. Hardin et al. (1993) reported the process for convert linear C5 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 of 150 to 600 ^{o}C. Cruze et al. (1994) the kinetics of liquid-phase dimerisation of 2-methyl-1-butene and 2-methyl-2- butene mixture catalysed by 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 with increasing temperature and molecular weight of the alcohol, except for methanol. Secondary alcohols showed higher dimers formation than that of primary alcohols. 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. Langmuir-Hishelwood-Hougen-Watson (LHHW) and Eley–Rideal (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 three active sites took part in the rate-limiting step of dimerisation, with an apparent activation energy for the dimerisation reaction in the range of 34–53 kJ mol^{-1}. Shah and Sharma () reported the first study of isoamylenes oligomerization using a macroporous acid resin catalyst, Amberlyst 15, and an acid-treated clay in the temperature range of 333–373 K. A first-order kinetics based on isoamylenes concentration was fitted, and a possible mechanism was explained on the basis of a Eley–Rideal theory for both catalysts. The yield of higher oligomers was only 2–3%, even at an isoamylenes conversion of 90%. Bricout et al. (1978) had reported the isomerization of olefins in a two-phase system (i.e., gas and liquid) catalyzed by nickel catalyst.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 for olefin control in FCC gasoline without loss in octane number. The use of different catalysts supported on composite carriers. The content in triple-zeolite (ZSM-5, Mordernite, H-Beta). carriers was found to be an important factor affecting the acid properties, pore structure, and hence hydroisomerization and aromatization activities of the catalysts. The ratio of Hβ to HMOR (modernite) was 2.5; the highest activity could be achieved. 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. Paivi et al. (2003) had studied effect of MeOH/2M1B feed 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 with the decreased of MeOH/2M1B feed molar ratio. A kinetic model based on three active sites gave the best fit, however the basic Langmuir-Hinshelwood (LH) mechanism might be adequate. Linnekoski et al. (1996) reported etherification reaction of isoamylenes (2M1B, and 2M2B) with methanol, ethanol, and n-propanol using a commercial ion-exchange resin amberlyst-15 as a catalyst. The different alcohols 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 model was developed that the adsorption of ethanol and olefins is not competitive. Alcohol adsorbs first, and then olefins and ether 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, comparable to the earlier obtained values. Vora et al. (1994) combined an etherification process to 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.

3.4 Simulations Program

Other applications of simulation program can be found in many processes such as methyl acetate process, MTBE Doherty et al. (1997) and ETBE Itoh et al. (2001). Since an effect of operating conditions and design parameters on the performance of reactive distillation can be investigated via simulation, there are many simulation studies on reactive distillation for ether synthesis. Sneesby et al. (1997) studied the simulation for ETBE synthesis in reactive distillation focusing on the design aspects. Moreover, Quitian et al. (1999) proposed a process of industrial production of ETBE by using ASPEN PLUS program. Also, Sahapatsombud et al. (2005) had been using Aspen plus to investigate and design reaction between ethanol and tert-amyl alcohol. This research related to design reactive distillation and study kinetic of the reaction that production of tert-amyl ethyl ether. Some researchers focused on the equilibrium simulation. Boyd et al. (1986) 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. The model can applied to handle chemical and physical equilibrium up to three multicomponent phases, and 15 components. Later, Mcdonald et al. (1985) examined the problem when the liquid phase is adequately modeled by the Non-Random two liquid (NRTL) activity coefficient expressions and the vapor phase is assumed to be ideal.

Only one research focused on etherification of FCC gasoline with alcohol. Andrzej et al. (1995) had been presented the thermodynamic analysis for etherification of FCC light 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 isomerization reaction of olefins and ethers were assumed do not take place. Because there are no thermodynamic data for C7 olefins and C6-C8 ethers. Two group contribution methods i.e., 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 than that in liquid phase due to phase reversion. Finally, the results from two group contribution method are similarly.

3.5 Group contribution method

Group contribution methods are widely used to predict many thermodynamic properties. Their advantages are that they need no experimental data, and since organic compounds used in chemical industry. Group contribution methods can be applied to really a great number of substances. However, most of group contribution methods have a serious problem that they cannot distinguish among structural isomers, because the isomers have the same number and kind of groups. The second order groups have been introduced into the group contribution equation. Iwai et al. (1999) introduce the second order of group contribution method for calculate normal boiling point of many substance. This method showed the absolute average error of the normal boiling points is 1.24 K. The proposed method can distinguish the normal boiling points of alkane isomers well. The saturated vapor pressures have been calculated using the present second order groups. The absolute average percent errors are 6.0, 3.6, and 6.0% at Tb−50, Tb and Tb+50, respectively. Benson et al. (1976) had proposed additives of molecular properties. It is shown that the zero-order approximation is equivalent to the law of additive of atomic properties, the first-order approximation to the law of additives of bond properties, the second-order approximation to the law of additives of group properties. The results showed agreements for the various additivity rules and certain extensions and limitations. The estimation of bond dissociation energies is possible with the additives rules as are the thermodynamic properties of free radicals. The conclusion showed that for Cp and S° (ideal gases), the additives of atomic properties works to about ±2 cal/mole-°K, while the additives of bond properties is usually good to about ±1 cal/mole-°K. The latter also estimates H_f^o to about ±3 kcal/mole. The group additives relation is generally obeyed to within ±0.5 cal/mole-°K for Cp and S° and about ±0.6 kcal/mole for H_f^o. Constantinou et al. (2004) had reported the expectation of higher order of group contribution method should be more correct than lower order group contribution method. The methods for prediction of normal boiling point, normal melting point, critical pressure, critical temperature, critical volume, standard enthalpy of vaporization at 298 K were investigated, standard Gibbs energy, and standard enthalpy of formation at 298 K. This research had showed to distinguish among isomers. Compared to the currently-used methods-first order method, this technique (Gani’s method) demonstrates significant improvements in accuracy and applicability. Dalmazzone et al. (2006) applied Benson's second order groups, for the prediction of critical temperatures and enthalpies of vaporization of covalent compounds. The results were compared to the most common existing first or second order group contribution methods. The overall precision for Tc predictions of 381 compounds is 5.8 K, which better than Constantinou of 9.2 K and Joback of 23.6K. The precision for prediction of ΔHvap of 319 compounds, at 298 K and at the normal boiling point. Furthermore, group contribution may now be used for the computation of gas phase properties, Tc, and ΔH_{vap} at any temperature lower than T_c. Rajagopal et al. (2005) estimated the standard enthalpy of formation, by Benson’s group contribution, and by semi-empirical molecular simulation methods compared with experimental data. Benson's method can estimate hydrocarbon enthalpies satisfactorily. The Benson's estimates of enthalpies of free radicals superior to the molecular simulation parameterization method (PM3) and are less accurate than the specialized computationally intensive PM3-family correlation (PM3-FC) method. The estimation of enthalpies for hydrocarbon radicals is substantially improved by a linear correlation of estimated values from semi-empirical molecular simulation method PM3 with experimental data. The radical enthalpies are now comparable to molecular simulated PM3-FC estimates. The hydrocarbon cations were divided into classes and estimated enthalpies found by adding Benson's enthalpy of radicals to the average ionization energy for the class. These predictions have an average absolute deviation of 8.6 kcal mol^{-1}. The proposed correlations effectively predict the standard enthalpy of formation of hydrocarbons, free radicals and carbocations. This methodology can be readily implemented in simulation programs to estimate thermochemical properties of hydrocarbons, free radicals and carbocations and to improve the design and optimization of hydroprocessing units reducing costly hydrogen consumption. Albahri et al. (1988) had used the group contribution method to predict the octane number of pure hydrocarbon liquid. It uses only chemical molecular structure to propose 200 pure hydrocarbon liquids. This research had applied the Joback’s group contribution method to estimate the pure-component octane number. In addition, the method had potential advantage of synthesis of additional hydrocarbon with knock measurements as a major objective. George et al. (1976) had use Ambrose, Joback and Chueh-Swanson definitions of group contributions and modified to account for the location of the functional groups in the molecule for predicting the auto ignition temperature (AIT) of pure components is presented The result proposed that method can predict the auto ignition temperature of pure components only from the knowledge of the molecular structure, with an average error of 2.8 % and a correlation coefficient of 0.98. Mavrovouniotis et al. (2004) had presented for the estimation of the standard Gibbs energies of formation of biochemical compounds (and hence the Gibbs energies and equilibrium constants of biochemical reactions) from the contributions of groups. The method employs a large set of groups and special corrections. The contributions were estimated via multiple linear regressions, using screened and weighted literature data. For most of the data employed, the error is less than 2 kcal/mol. The method provides a useful first approximation to Gibbs energies and equilibrium constants in biochemical systems.

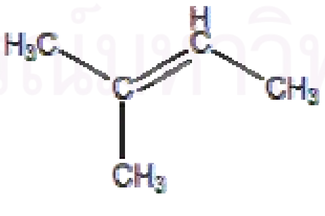
CHAPTER IV

RESEARCH PROCEDURE

This chapter describes the experimental procedure for the improvement of the fuel oil quality by the etherification of FCC gasoline with ethanol in simulation and experiment. It is divided into four parts; Selection of group contribution method, simulation program etherification of FCC gasoline with pure ethanol and the etherification and hydration of FCC gasoline with water/ethanol azeotropic mixture.

4.1 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 can be classified into 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 can be described as follows; 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 4.1. The molecular structure of 2-methyl-butene

Tabel 4.1 The number of subgroup unit from difference method

Subgroup type	Ambrose’s	Joback’s	Gani’s	Bensons’s
First order group				
Alkyl carbon	5	-	-	-
>C<	1	-	-	-
>CH-	1	-	-	-
Double bond	1	-	-	-
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	Ambrose’s		Joback’s			Gani’s		
	Tc	Pc	Tc	Pc	Tb	Tc	Pc	Tb
Alkyl carbon	0.138	0.226	-	-	-	-	-	-
>C<	-0.12	-0.03	-	-	-	-	-	-
>CH-	-0.043	-0.006	-	-	-	-	-	-
Double bond	-0.05	-0.065	-	-	-	-	-	-
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. (2004) or from literature. In this research, the example for 2-methyl-2-butene is showed in Table 4.3 and Table 4.4.

Table 4.3 The value of subgroup unit from difference method

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.

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

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

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

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

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

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

$$S_s^o = 8.314*[0] = 0 \text{ J/ mol K}$$

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

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

$S^o (298.15K) =$ {(3*127.29) + (1*-53.16) + (1*33.36)} = 362 J/mol K =0.362 kJ/mol K.

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

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

4.2 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 showed in Appendix E. The molecular structure should be import from other source because Aspen plus program define the difference molecular, program define the possible structure are contained in program. In this research will be applied the Chemdraw program to create the new molecular structure. The type of file from Chemdraw program must be mole file (.mol). Anyway, the functional groups of each component of several methods are listed in Appendix A-D. The properties of components that estimated by Aspen plus program will be brought to compare with the data from handbook. The weight fraction of component remain in product feed will be brought to compare with the weight fraction remaining of component from experiment.

4.3 Equipment and chemical

4.3.1 Batch Reactor Apparatus

The reaction was carried out in a cylindrical shape autoclave type reactor. The 100 cm^3 reactor was maintained at a constant temperature by circulating hot water in jackets as shown in Figure 4.2. The turbine was used to stir the mixture at the maximum speed of 1163 rpm in all experiments to minimize the external mass transfer resistance. The reactants were placed into the batch reactor with 10 g of catalyst at the room temperature. A valve for liquid sampling and a port for the thermocouple were installed at the top. The system was pressurized by N_2 at 0.8 MPa to ensure that all reaction components were in the liquid phase. It should be noted that the reaction is not occurred without heating (Rihko et al., 1998).

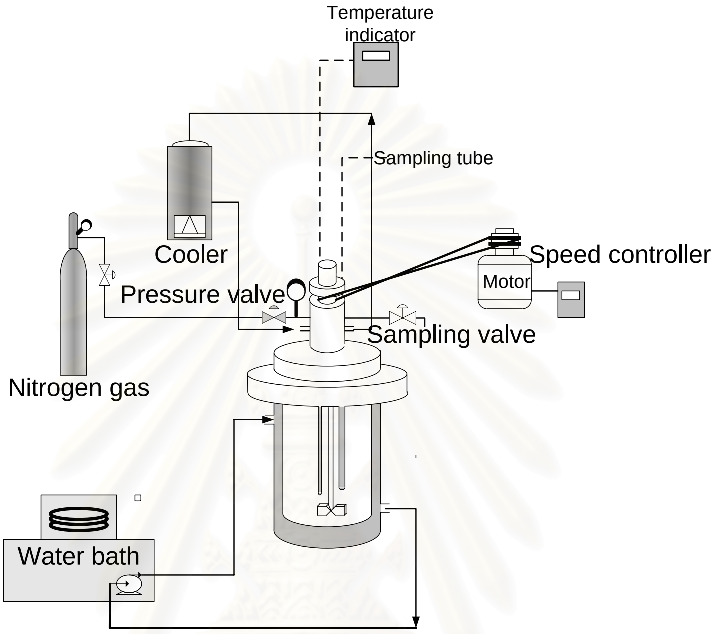


Figure 4.2 Batch Reactor Apparatus

4.3.2 Chemical

The chemicals used in this study consist of standard grade chemicals with purity higher than 99.5% for gas chromatograph calibration and reagent grade chemicals for major experiments. Table 4.5 provides the details of chemical purity and suppliers. And Table 4.6 showed the compositions of FCC light gasoline.

4.3.3 Catalysts

This study was the catalyst screening for the fuel oil quality improvement by the etherification of FCC gasoline with pure ethanol. The strong acid ion exchange resin, Amberlyst 15, is the strong acid ion exchange resin that the pore size type is macrorecticular pore. The catalysts were dried overnight in an oven at 383 K before use.

Table 4.5 Details of chemicals use in the study

Chemical materials	Purity (%)	Supplier
Standard grade		
IA	> 99.5	Chemika Fluka
TAEE	90	Laboratory
Industry grade		
FCC gasoline	ND	Thaioil Public Company Limited
Reagent grade		
Water	100	Laboratory
EtOH	> 99.5	SR lab

Table 4.6 Physical properties of catalysts

Catalysts	Supplier	Ion Exchange Capacity (meqH$^+$/kg Catalyst)	Surface Area (m^2/g)	Pore Diameter (nm)	Pore Volume (cm^3/g)
Amberlyst 15	Chemika Fluka	5.0	900	1000	1.82

Table 4.7 FCC light gasoline composition (mass percent)

	n-parafin	i-parafin	olefins	naphtenes	aromatics	oxygenate	total
c4	0.347	0.205	1.655	0	0	0	2.207
c5	0.908	6.911	7.891	0.115	0	0	15.825
c6	0.74	7.021	6.575	1.881	0.403	0	16.619
c7	0.721	5.812	5.959	3.129	2.83	0	18.451
c8	0.901	4.659	1.133	3.969	5.943	0	16.605
c9	0.276	3.968	0.634	2.61	5.923	0	13.411
c10	0.25	3.245	0.212	0.621	3.34	0	7.668
c11	0.136	1.356	0	0.231	1.537	0	3.261
c12	0.048	0.14	0	0.054	0.379	0	0.621
c13	0.015	0	0	0	0	0	0.015
total	4.34	33.317	24.06	12.61	20.356	0	94.683

* Technique supported by Thai Oil Company.

4.4 Experimental procedure

1. The solution was pressurized by N_2 gas to 0.8 MPa to prevent vaporization of liquid solutions. and stirred at about 1163 rpm.

2. To study ethanol volume, the reaction system consisted of FCC gasoline and pure ethanol with a volume ratio of 80:20, 70:30, 40:60 and 50:50 vo% , and volume ratio of 90:10, 80:20, 70:30, 50:50 for azeotropic mixture of ethanol/water with 10 g of catalyst, and heated to the desired reaction temperature (343 K) for 24 h.

3. To study effect of temperature, the reaction system consisted of FCC gasoline and pure ethanol with a volume ratio of 70:30 with 10 g of catalyst and heated to the desired reaction temperature are 60, 70, 80, and 90 ^{o}C for 24 h.

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 24 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.

4.5 Analysis

Chemical compositions of a liquid sample were analyzed by using a gas chromatograph. The analysis was done by injecting 1 μl of sample in the column. The amount of ethanol was further analyzed by Shimadzu GC 8A with helium gas as carrier gas. The injector temperature and the detector temperature were set at 200 and 220 ^{0}C, respectively.

Table 4.8 Operating conditions of gas chromatography Shimadzu GC8A

Gas Chromatography Shimadzu GC8A					
Operating Conditions		**Intergration Parameter**			
Detector	TCD	Width (sec)	5	Slope (uV/min)	30
Carrier Gas	He (99.98 %)	Drift (uV.min)	0	T. DBL (min)	1000
Carrier Gas Flow rate (cm3/min)	30	Stop Time (min)	35	Atten (2^X mV)	5
Packed Column	Gaskuropack 54	Speed (mm/min)	2		
Length of Column (m)	2.5	**Quantitative Parameters**			
Mesh size of Packing	60/80	Method (0-8)	1	Curve (Calib. Fit Type)	0
Injection temperature (K)	443	Cal. Levl (0-15)	1	Min.Area (count)	100
Column temperature (K)	473	Win. Band (0:win 1: Band)	0	Window (%)	5
Detector temperature (K)	473	Spl. Wt	100	IS. Wt	0
Current (A)	80	Dilfact	1		

CHAPTER V

RESULTS AND DISCUSSION

In this chapter, group contribution methods (i.e. Joback's, Gani's, Ambrose's and Benson's method) are investigated for estimating the missing properties of components. In this study, the predicted properties from Joback's, Gani's and Ambrose's methods were compared for the critical properties (i.e. critical pressure and critical temperature). Joback's method, Gani's method and Benson's method were used to estimate the Gibbs of formation. Later, the group contribution method was added to Aspen Plus program and the effect of ethanol volume and temperature on etherification reaction was investigated. Lastly, the isomerization of olefins was taken into account. The simulation results and experimental results were compared and discussed.

5.1 Group Contribution

This section will be compared various group contribution methods: Ambrose's method, 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.

5.1.1 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 but Gani's method is a combination of first order and second order group contribution method. 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 5.1. The result showed that the predicted normal boiling points from both Joback's method and Gani's method are in good agreement with the values from literatures.

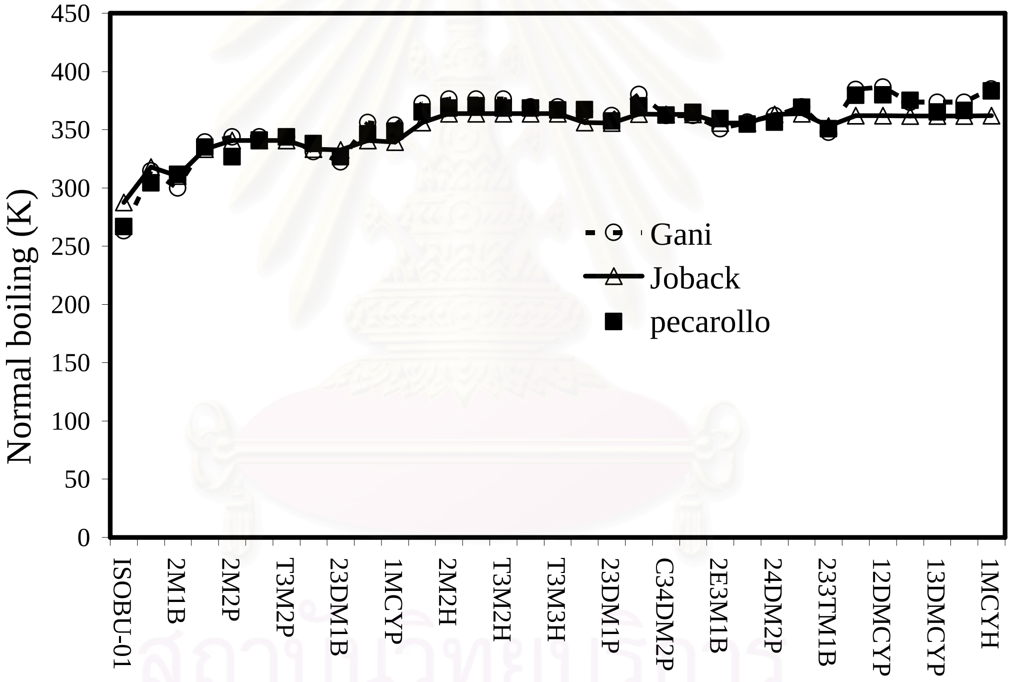


Figure 5.1 Normal boiling of reactive olefins

Figure 5.2 shows the normal boiling of oxygenates from Joback's method and Gani's method. Both methods show the similar results. Therefore, either Joback's or Gani's methods can be used for estimating the normal boiling point. The precision of result from both methods are slightly different. However, the first order group contribution method is less complex than first-second order and second order method.

Conclusively, Joback’s method is more preferable for estimating normal boiling point of reactive olefins and oxygenates.

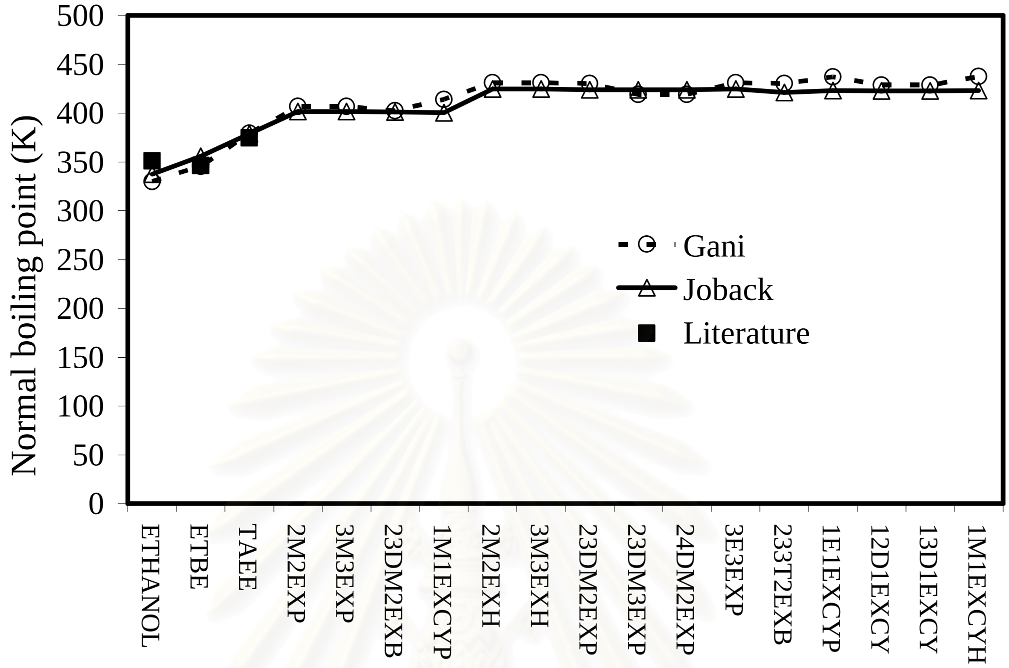
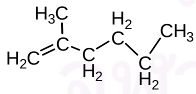


Figure 5.2 Normal boiling of ethanol and ether products

Table 5.1 The subgroup from Ambrose’s, Joback’s and Gani’s group contribution method for calculating critical properties

Component	Group method	Subgroup				
		First order				Second order
	Ambrose’s	Alkyl carbon	>C<	Double bond	-	-
	Joback’s	CH3(1)	CH2(2)	CH2=(1)	C=(3)	-
	Gani’s	CH3(1)	CH2(1)	CH2=C(2)	-	CH3-Hm=CHn m,n(0,2)

An example of 2-methyl-1-hexene in C7 olefin is investigated. The numbers of subgroups and its value from different group methods are shown in Table 5.1 and 5.2, respectively. The obtained normal boiling points are 372.34 K, 356.12 K and

365.1 K from Gani’s method, Joback’s method and Pescarollo et al., (1993) respectively.

Table 5.2 The values of subgroup group from Joback’s and Gani’s group contribution method for calculating normal boiling point

Subgroup type	Joback’s	Gani’s
	Tb	Tb
CH3(1)	23.58	-
CH2(2)	22.88	-
CH2=(1)	18.18	-
C=(3)	24.14	-
CH3(1)	-	0.8894
CH2(2)	-	0.9225
CH2=C(2)	-	1.7117
CH3-Hm=CHn m,n(0,2)	-	0.0668

5.1.2 Critical properties

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

The example of counting subgroup for critical temperature with different group contribution methods was shown in Table 5.3. The results show that the critical temperature of 2-methyl-1-hexene is 609.8K, 526.4K, 541K and 538K for Ambrose’s method, Joback’s method, Gani’s method and literature, respectively. The critical temperatures differences from literatures are 71.8K, -11.6K and 3K, respectively. The results of the other components presented in Appendix F shows the similar results to that of 2-methyl-1-hexene, Leonidas Constantinou and Gani suggested that the higher order of group contribution method predicts more reliable results than the lower order. In this case, Ambrose’s methods showed less accurate than other methods.

Table 5.3 The values of subgroup from Ambrose's, Joback's and Gani's group contribution method for calculating critical properties

Subgroup type	Ambrose's		Joback's		Gani's	
	Tc(K)	Pc(bar)	Tc(K)	Pc(bar)	Tc(K)	Pc(bar)
First order group						
Alkyl carbon	0.14	0.23	-	-	-	-
>C<	-0.12	-0.03	-	-	-	-
Double bond	-0.05	-0.07	-	-	-	-
CH3(1)	-	-	0.0282	-0.0012	-	-
CH2(2)	-	-	0.0567	0	-	-
CH2=(1)	-	-	0.0113	-0.0028	-	-
C=(3)	-	-	0.0117	0.0011	-	-
CH3(1)	-	-	-	-	1.6781	0.0199
CH2(2)	-	-	-	-	3.4920	0.0106
CH2=C(2)	-	-	-	-	6.5081	0.0223
Second order group						
CH3-CHm=CHn m,n(0,2)	-	-	-	-	0.0167	-0.00018

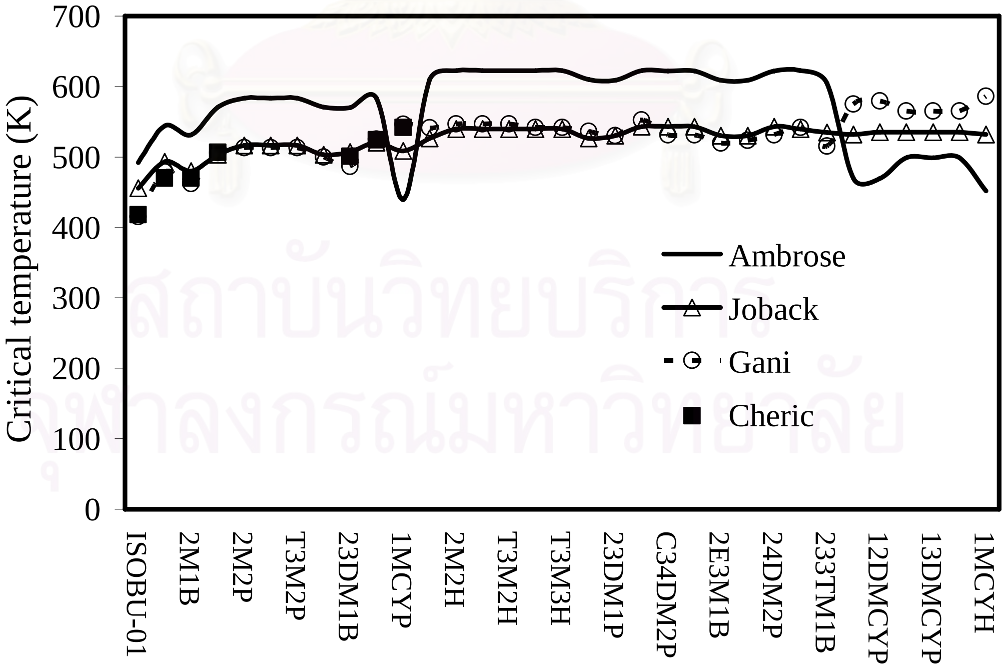


Figure 5.3 Critical temperature of reactive olefins

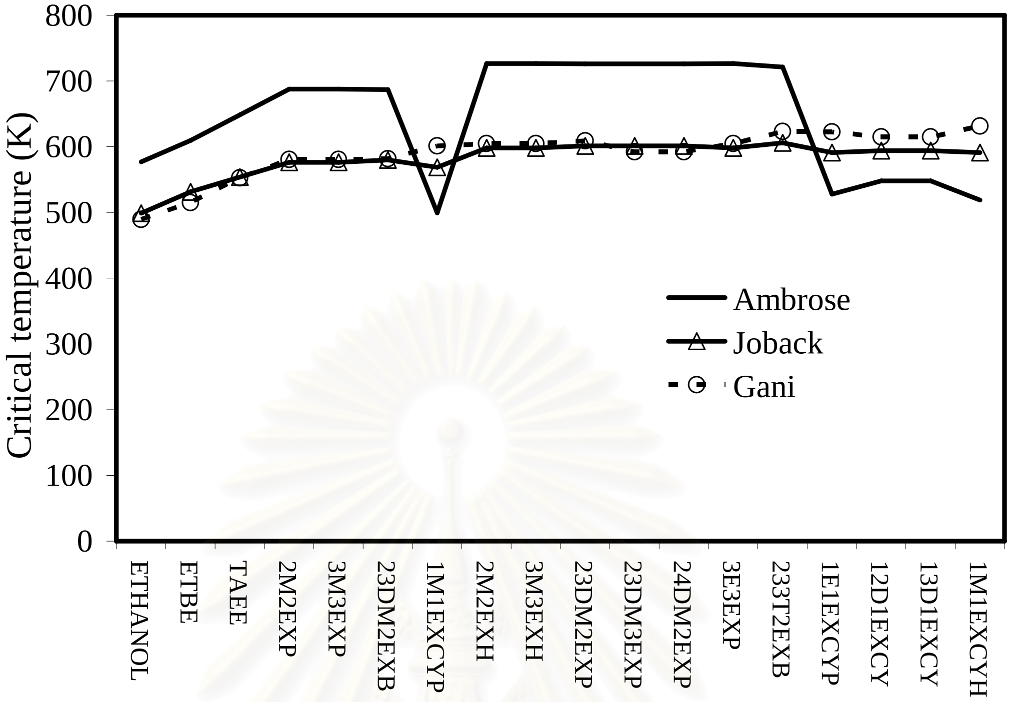


Figure 5.4 Critical temperature of ethanol and ether products

Figure 5.4 presents the critical temperature of oxygenates. Similarly, the same trend can be observed in oxygenates compounds. However, it should be noted that no available data of oxygenates is currently present.

For calculation of critical pressure, Gani’s method, Joback’s method and Ambrose’s method can be applied. The results of obtained critical pressure are 30.4 30.8, 26.69 and 28.32 atm for Ambrose’s method, Joback’s method, Gani’s method and literatures, respectively. The deviation result for various group contribution methods are 2.08, 2.48 and 1.63 atm for Ambrose’s, Joback’s and Gani’s method, respectively. Similar to other components as shown in Figure 5.5 and Figure 5.6, the results show that Gani’s method is more slightly accurate than other methods.

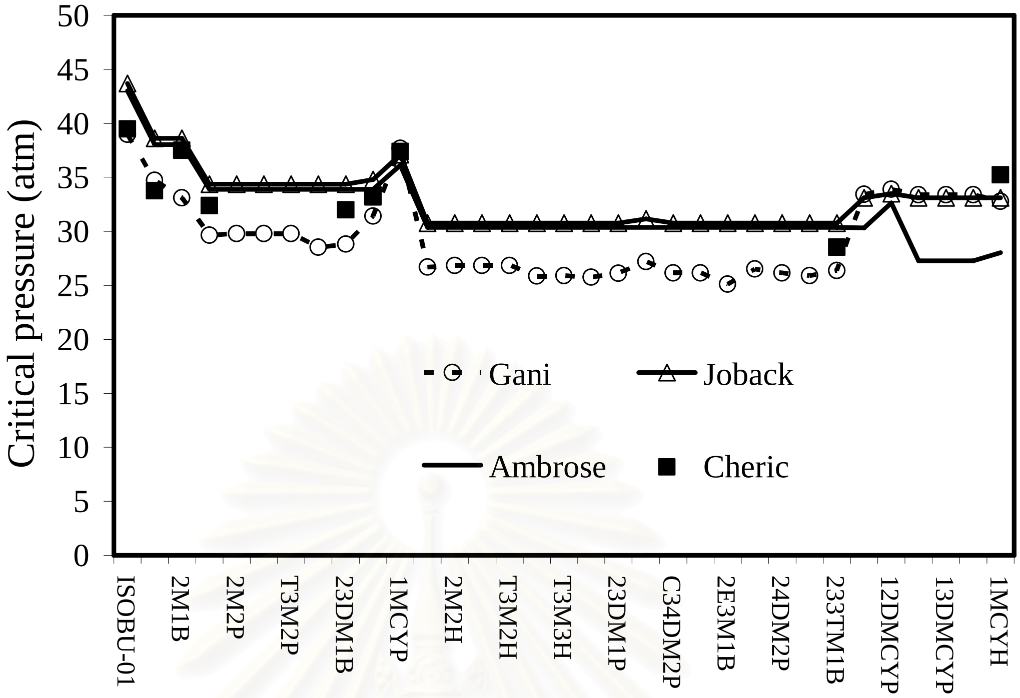


Figure 5.5 Critical pressure of reactive olefins

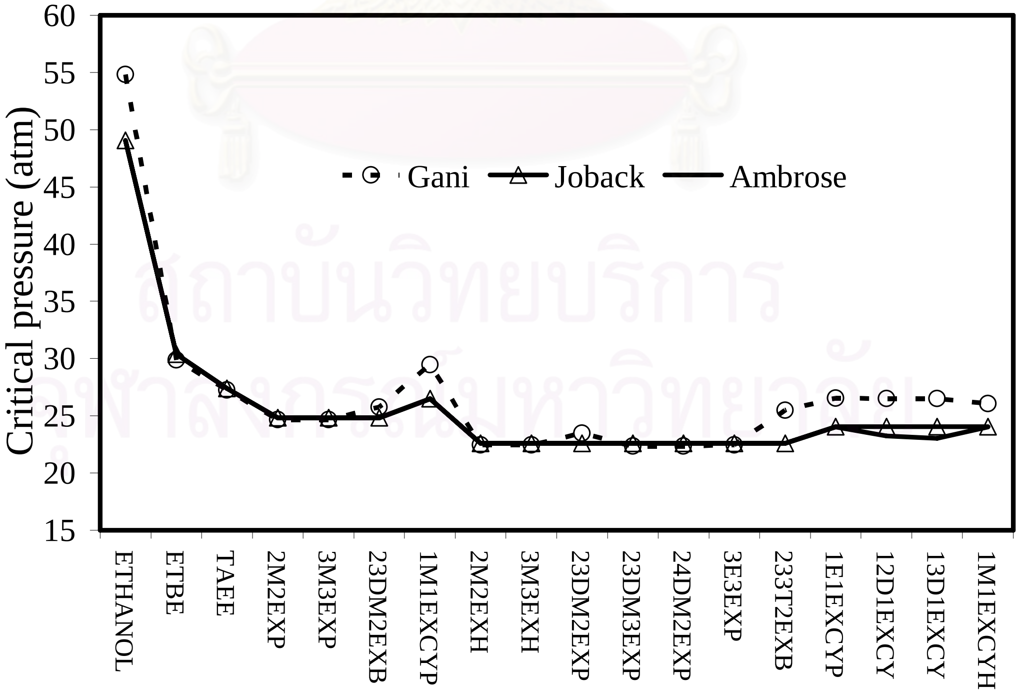
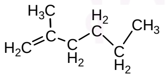


Figure 5.6 Critical pressure of ethanol and ether products

5.1.3 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 thermochemical data computation. Even so, a much greater number of contributions is needed. Table 5.4 illustrates subgroup of 2-methyl-1-hexen from Joback’s, Gani’s and Benson’s method as presented in Appendix D. 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 5.7.

Table 5.4 The subgroup from Joback’s and Gani’s and Benson’s group contribution method for calculates Gibbs free energy of formation

<table>
<tr><th>Component</th><th>Group method</th><th colspan="8">Functional group</th></tr>
<tr><td rowspan="5"></td><td colspan="9">First order</td></tr>
<tr><td>Joback’s</td><td colspan="2">CH3(1)</td><td colspan="2">CH2(2)</td><td colspan="2">CH2=(1)</td><td colspan="2">C=(3)</td></tr>
<tr><td>Gani’s</td><td colspan="2">CH3</td><td colspan="2">CH2</td><td colspan="2">CH2=C</td><td colspan="2">CH3-Hm=CHn m,n(0,2)</td></tr>
<tr><td colspan="9">Second order</td></tr>
<tr><td>Benson’s</td><td>CH3-(C)</td><td>CH2-(2C)</td><td>CH3-(=C)</td><td>CH2=</td><td>=C-(2C)</td><td>CH2-(C,=C)</td><td>Optical isomer</td><td>Total symmetry</td></tr>
</table>

Joback’s method shows the most deviation of the Gibbs energy (10.4 kJ/mol) from unity. Benson’s method and Gani’s method show the results close to the values from literatures (~3.24 kJ/mol). Many researches have been attempting to develop the group contribution method to classify the isomer structures of molecules (Iwai et al., (1999); Dallmazzone et al., (2006); Constantinou et al., (2004)). From Appendix C, Gani's shows the similar subgroup for isomers; therefore, structural isomers cannot be distinguished. On the other hand, Benson's method shows all significantly different subgroup for all components.

According to Kitchaiya et al. (1996)'s work, the results of TAEE available in the TRC Thermodynamic Tables (1992) were compared with those of experimental. The results found the significant difference because the Gibbs free energy of formation was found only in gas phase but the experiment was controlled in liquid phase.

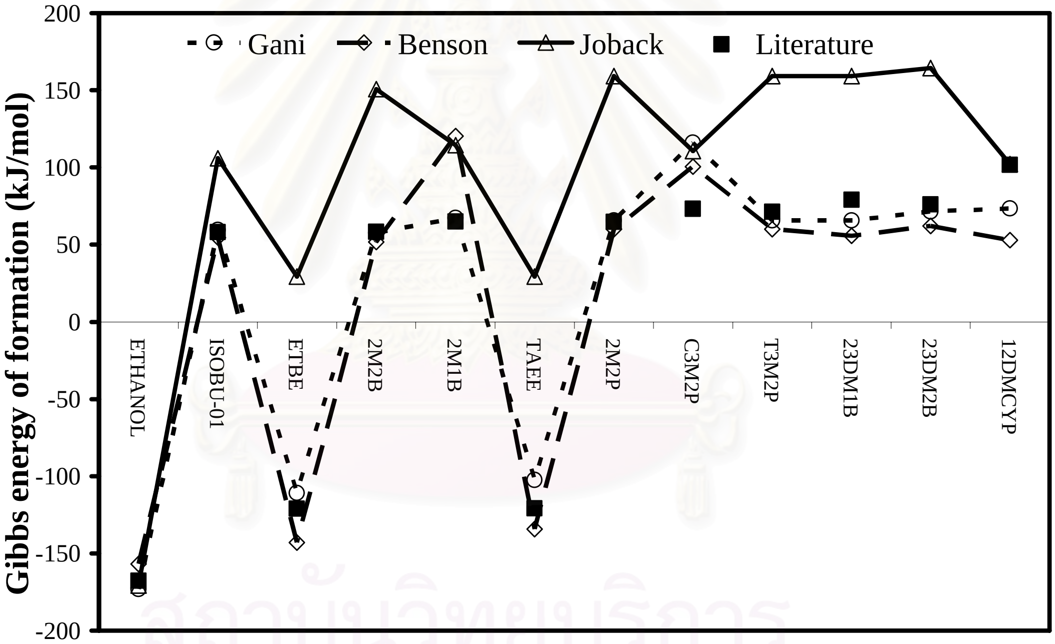
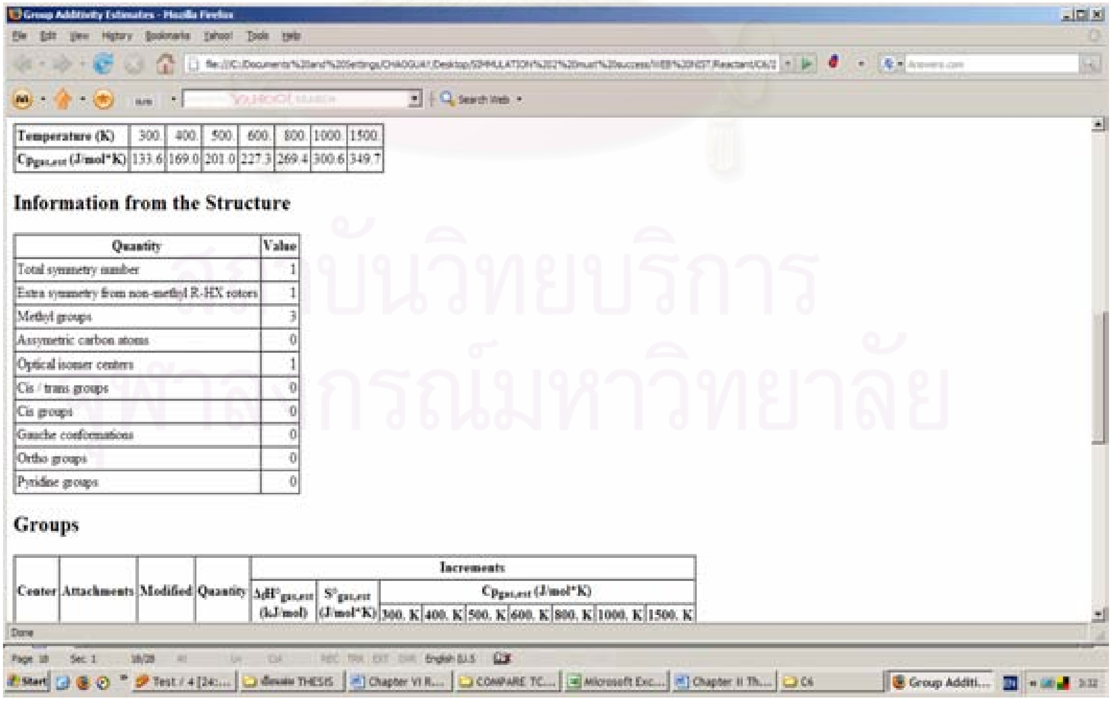


Figure 5.7 Gibbs free energy of formation of reactive olefins and ether products

Table 5.5 The values of functional group from Benson's, Joback's and Gani's group contribution method for calculating Gibbs free energy of formation

Subgroup type	Benson's	Joback's	Gani's
CH3-(C)	-	-	-
CH2-(2C)	-	-	-
CH3-(=C)	-	-	-
CH2=	-	-	-
=C-(2C)	-	-	-
CH2-(C,=C)	-	-	-
Optical isomer	-	-	-
Total symmetry	-	-	-
CH3(1)	-	-43.96	-
CH2(2)	-	8.42	-
CH2=(1)	-	3.77	-
C=(3)	-	92.36	-
CH3(1)	-	-	-8.030
CH2(2)	-	-	8.231
CH2=C(2)	-	-	88.402
CH3-Hm=CHn m,n(0,2)	-	-	0.95

*Gibbs free energy of formation from Benson's method is calculated from eq 2.15



Temperature (K)	300.	400.	500.	600.	800.	1000.	1500.
$Cp_{gas,est}$ (J/mol*K)	133.6	169.0	201.0	227.3	269.4	300.6	349.7

Information from the Structure

Quantity	Value
Total symmetry number	1
Extra symmetry from non-methyl R-HX rotors	1
Methyl groups	3
Assymetric carbon atoms	0
Optical isomer centres	1
Cis / trans groups	0
Cis groups	0
Gauche conformations	0
Ortho groups	0
Pyridine groups	0

Groups

Center	Attachments	Modified	Quantity	Increments								
				$\Delta_f H^\circ_{gas,est}$ (kJ/mol)	$S^\circ_{gas,est}$ (J/mol*K)	$Cp_{gas,est}$ (J/mol*K)						
						300. K	400. K	500. K	600. K	800. K	1000. K	1500. K

Figure 5.8 The NIST featuring stereochemistry structures

According to the values of subgroup shown in Table 5.5, Benson’s method is excellent in predicting the properties of molecules. The standard Gibbs free energy of formation calculated from Eq 2.15 is not a sum of standard Gibbs free energy of subgroup. Therefore, the Gibbs free energy of formation of subgroup is not available. In addition, the details of stereochemistry structure must be included as it can be taken from NIST database. The details of stereochemistry, optical isomer, gauche and symmetry were applied to calculate of Gibbs free energy of formation using Benson’s group contribution method. The information of structure in NIST database is shown in Figure 5.8. If the component does not exist in the database, NIST allows you to upload the component structure (.mol) or drawing your structure in NIST website and upload it. The data shown in NIST are optical isomer, total symmetry, cis-trans structure, etc.

Conclusively, several of group contribution methods (i.e., first order, first-second order and second order) were used to estimate the missing properties such as critical properties, normal boiling point and standard Gibbs free energy of formation. Selection the most appropriate group contribution method for applying to Aspen plus program was investigated. For normal boiling point, the critical temperature and critical pressure, Joback’s method and Gani’s method are elegantly described. For Gibbs free energy of formation, it was previously expected that the second order group contribution method should yield the precise prediction. Nevertheless, the result found that Gani’s method yields the close estimation to the data from literatures. Overally, Gani’s method can perfectly describe normal boiling point, critical temperature, critical pressure and Gibbs free energy. However, Gani’s method cannot distinguish the isomer structure of some components. Hence, all three of group contribution methods (i.e. Joback’s method, Gani’s method and Benson’s method) were applied to Aspen Plus program.

Next, the module of RGibbs reactor in Aspen Plus simulator will be further studied. In this research, the reaction between reactive olefins from fluidized catalytic cracking with ethanol will be brought to investigate. In addition, the effects of reaction temperature and ethanol volume on equilibrium reactions were lastly examined.

5.2 Pure Ethanol

5.2.1. Effect of Ethanol Volume

The ethanol volume in feed is varied from 1 - 80 vol% at operating condition of 0.8 MPa, 70^{o}C. The effect of ethanol volume on ethanol remaining in product and weight fraction of C5 reactive olefins with different group contributions is presented in Figure 5.9 and 5.10, respectively. In Figure 5.9, three group contribution methods show differences of the remaining C5 reactive olefins from the experimental results whereas the results of the remaining ethanol are close to those of experimental data figure 5.9 and figure 5.10. For weight fraction of remaining C5 olefins, the difference between results from simulation and experiment can be observed. It can be explained that the weight fraction remaining of C5 olefins from experimental data is higher than that from simulation because the catalysts in experiments can help the isomerization or cracking reaction as explained in Corma et al. (1996) and Slomkiewicz et. al. (1997)'s work. Miller et al. (2001) reported that the isomerization reaction can occur in the range of temperature from 50-500 ^{0} C but it prefers to take place around 100 – 400 ^{o} C. In contrast, the results in Figure 5.10 showed slight differences in weight fraction remaining of ethanol between experiment and simulation. Fite et al. (1994) revealed that an increase of olefins conversion corresponds to a decrease of weight remaining in product. However, the regulations of ethanol volume for fuel specification are E10 (ethanol 7 wt %), E15 (11 wt%) and at present E20 (15 wt%). The results found that the maximum allowable volume of ethanol, which can be added to react with FCC light gasoline and will not violate the specification of E10, is 30 % vol as shown in Figure 5.10.

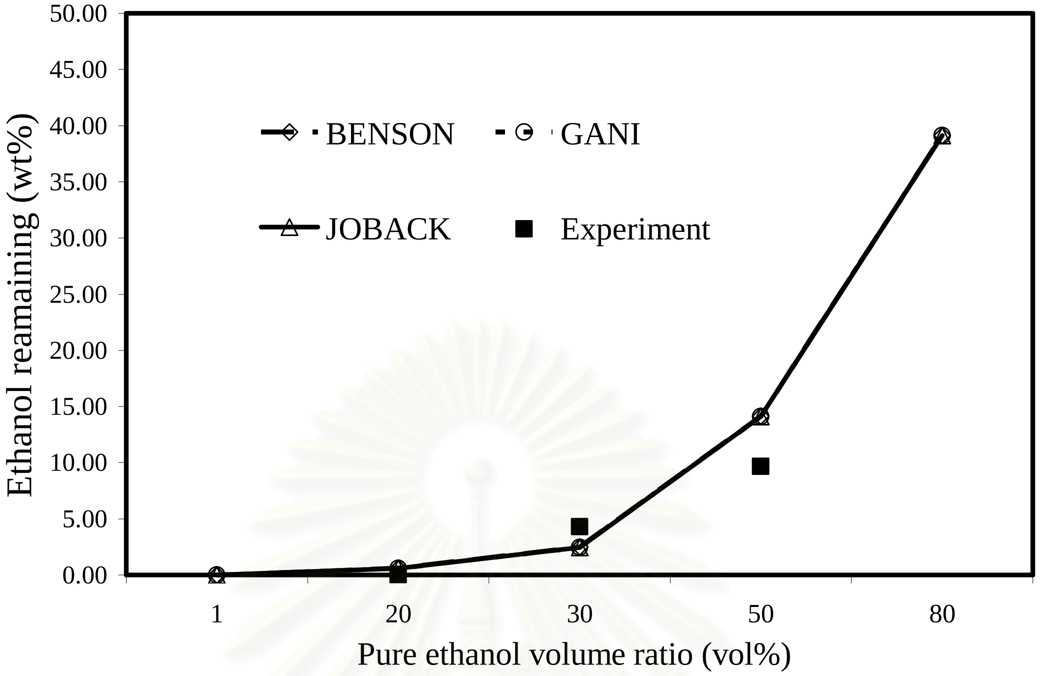


Figure 5.9 Weight of ethanol remaining in products at different ethanol volume

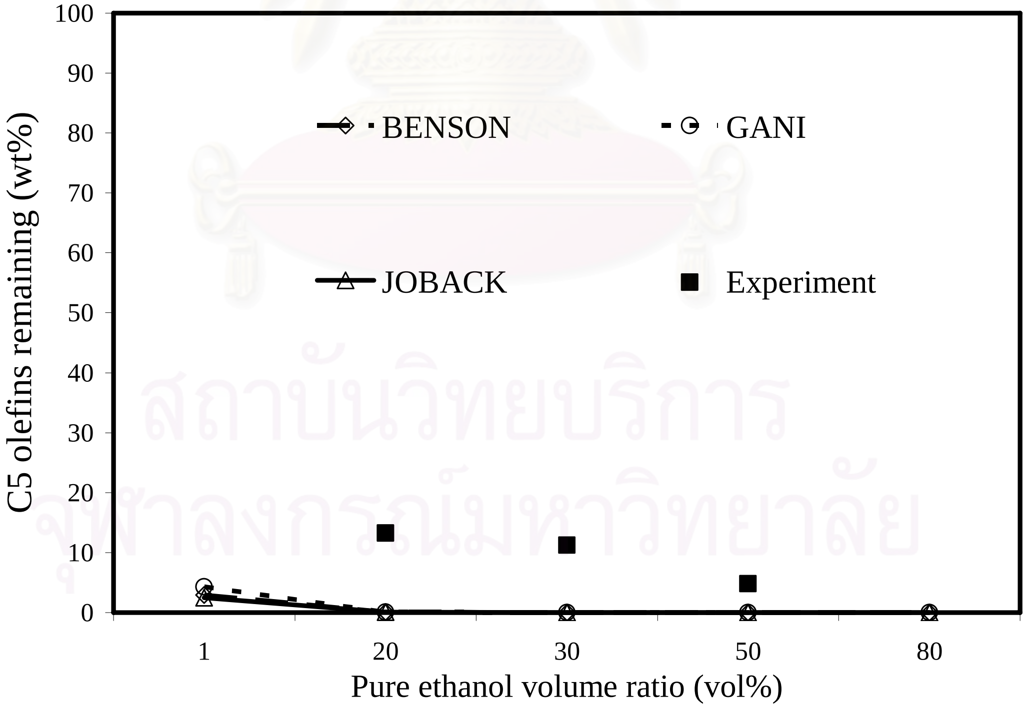


Figure 5.10 Weight of C5 olefin remaining in products at different ethanol volume

Furthermore, Thipsunet et al. (2006) reported that the higher ethanol volume ratio increases the olefin conversion and results in higher octane number in products. Also, the ether products also affect the vapor pressure. Various ethers such as ethyl-tert-butyl ether (ETBE) (Jensen et al., 1995 ; Oudshoorn et al., 1999; Fite et al. 1994), tert-amyl ethyl ether (TAEE) (Juha et al., 1994; Varisli et al., 2005), tert-hexyl ethyl ether (THEE) (Zhang & Ravindra Datta, 1996) are produced from the reaction. Because ethers have lower vapor pressure than alcohols, ethers are more preferable to be used for improving the octane number.

5.2.2 Effect of Temperature

The effect of temperature on weight of ethanol remaining in the products was illustrated in Figure 5.11. The ethanol volume fraction in feed is kept constant at 30 vol %. The reaction temperature is varied from 40 ^{o} C – 100 ^{o} C. As show in Figure 5.11 the experimental results shows weight of ethanol remaining increases with increasing temperature. This is because the etherification reaction is exothermic and results in the decrease of olefin conversion. It can be observed that the simulation results show the same trend for all three different group contributions. Moreover, the simulation results are in good agreement with the experimental data as shown in Figure 5.12. However, weight fraction of remaining olefins is obviously higher than that of simulation. It can be implied that isomerization of C5 reactive olefins reaction can be occurred as previously described. The isomerization takes place after a typical acid-catalyzed process involving the formation of carbonium ions produced by protonating the olefinic double bonds.

Although the simulation results showed the higher conversion of etherification reaction at lower temperature (50 - 60 ^{o}C), but many previous literature had reported experimental data shows isomerization reaction or cracking of linear paraffin/non-reactive olefins is more favorable at higher temperature. Also, this reaction must use the acidic catalysts and high temperature range 50 – 450 ^{o}C. The etherification reaction cannot take place without the catalysts as Thipsunet et al., (2006) had reported. Finally, the suitable temperature for etherification reaction is 70 ^{o} C.

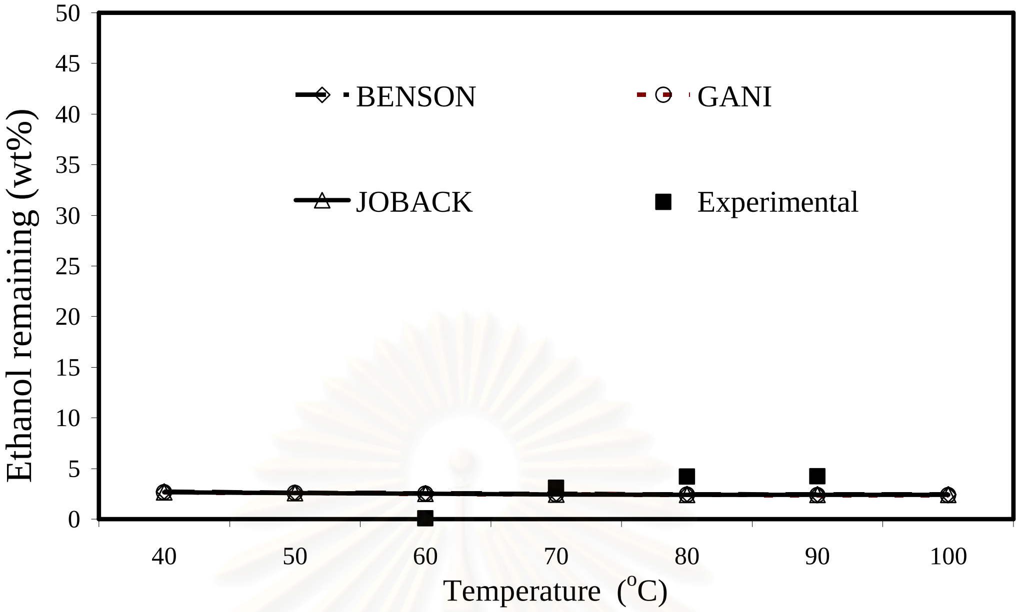


Fig 5.11 Weight of ethanol remaining in products at different temperatures

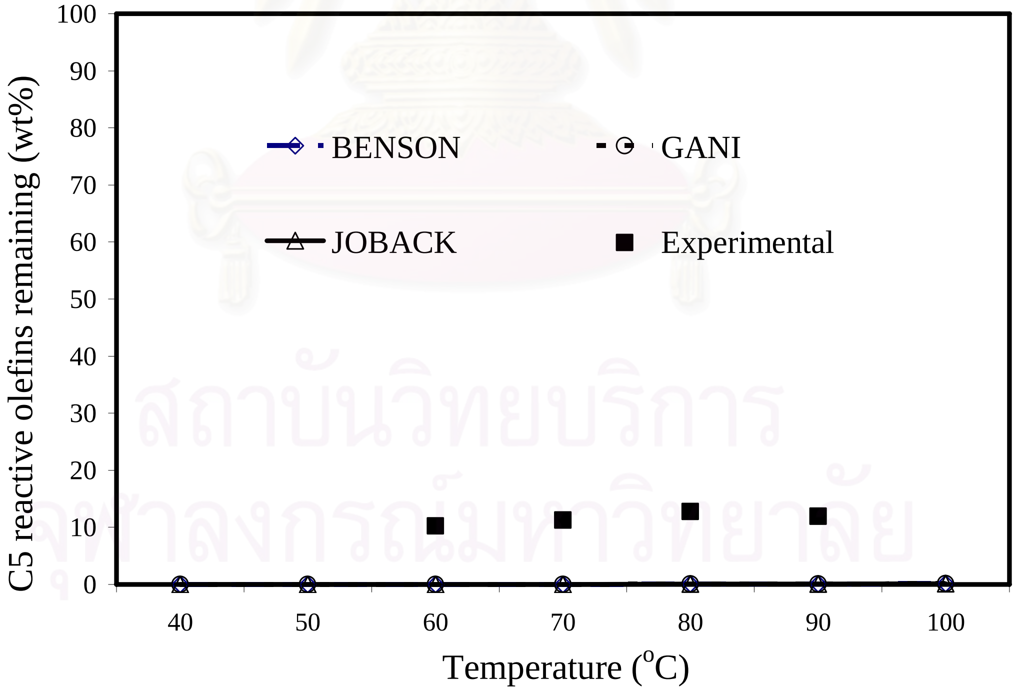


Fig 5.12 Weight of C5 olefins remaining in products at different temperatures

Furthermore, the isomerization of C4 olefins yields four isomers. The investigation of converting normal butane into isobutene was reported in Harding et al. (1993). Additionally, C5 olefins exist in five isomers. To produce olefins isomer products, the feedstock requires contact catalysts such as zeolite Miller et al. (2001) had reported, so that the isomerization reactions between reactive olefins such as 2M1B⇔2M2B, 23DM1B⇔23DM2B etc, was added to Aspen plus program. To investigate the effect of isomerization reaction, Benson's group contribution method was used because of more efficient distinguishing the isomer of reactive olefins. The results are shown in Figure 5.13 and Figure5.14. From Figure 5.13, it was found that the better results are obtained when the effect of isomerization reaction is included.

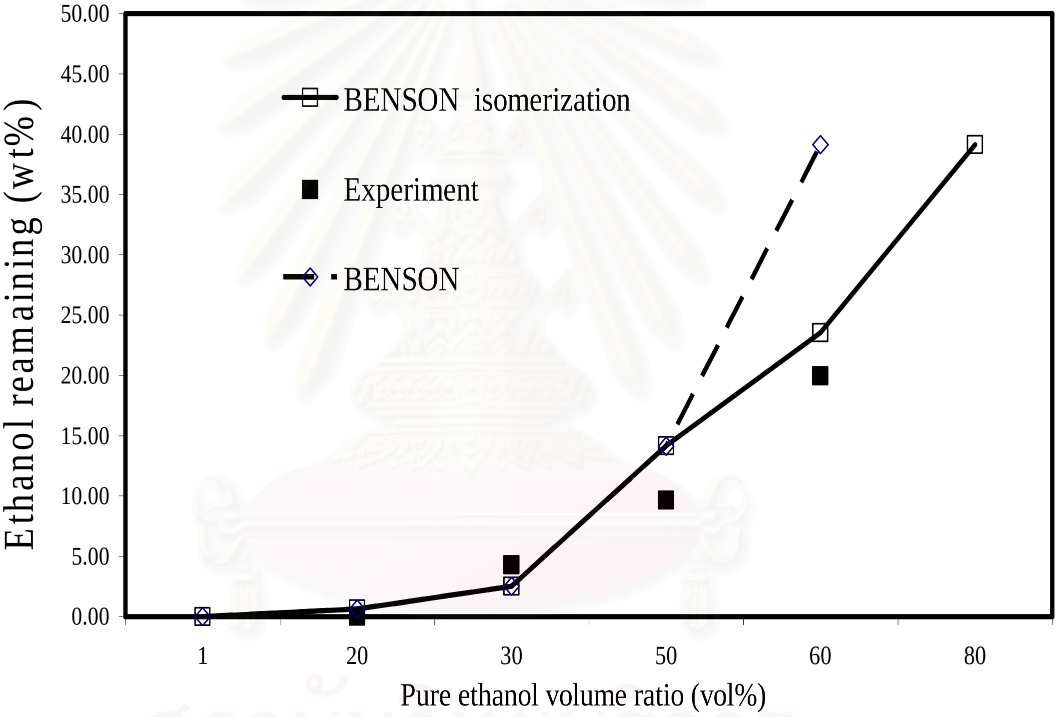


Figure 5.13 Weight of ethanol remaining in products when added isomerization

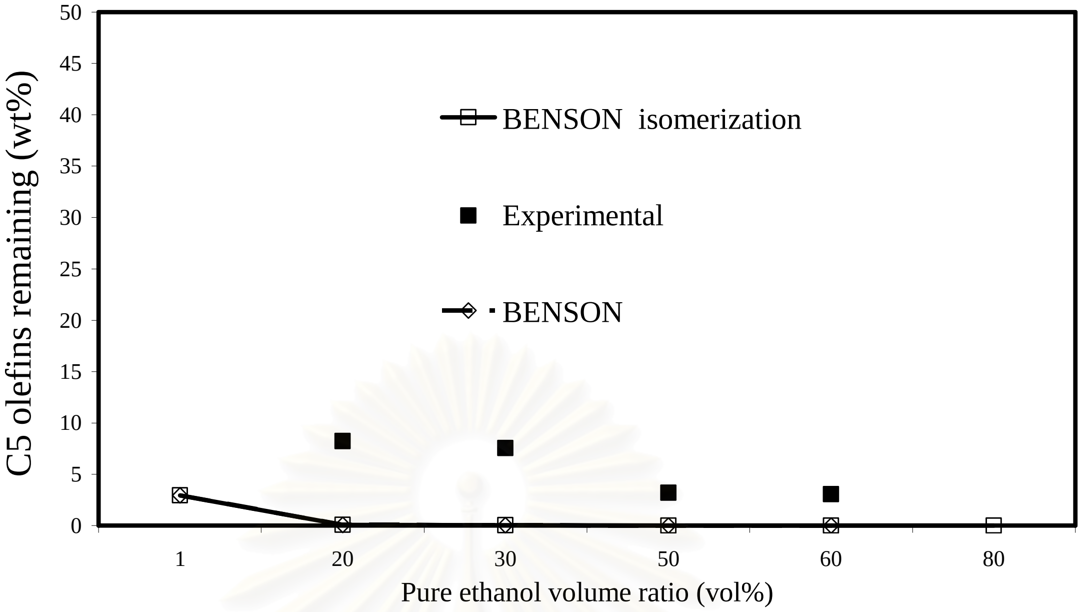


Figure 5.14 Weight of C5 reactive olefins remaining in products when added isomerization

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

This chapter contained the result conclusion of group contribution method**.** The optimum operating condition such as temperature and ethanol volume will be concluded.

6.1 Conclusions

6.1.1 Group contribution method

The group contribution methods for estimate thermodynamic properties and physical properties are Ambrose's method, Joback's method, Gani's method and Benson's method. Although, Joback's method and Ambrose method can be applied to estimate the properties but the most method for estimate critical properties and normal boiling point. Benson's method and Gani's method for estimation of standard Gibb's free energy of formation are well predicted. But Gani's method can not classify for some components because of the same of subgroup follow to appendix C. So, the recommendation for estimate standard Gibb's free energy of formation is Benson's method as a second order group contribution method. Also, the estimation the critical temperature, critical pressure, normal boiling point should be chosen by Gani's method. But sometimes the critical temperature, critical pressure and normal boiling point can be chosen Joback's method to decrease the complexity.

6.1.2 Effect of ethanol volume

Ethanol pure was added to react with FCC light gasoline for olefin reduction. This reaction can be reduced olefin content in fuel oil and improve octane number together. Furthermore, the increasing of ethanol volume will increase the olefin conversion. In addition, to restrict the amount of ethanol in fuel oil not exceed the specification of E10 so that volume of pure ethanol can be added 30 vol %. Nowadays, many cars had been proposed to accept the gasohol E20. So, it possible that adding more ethanol to react with FCC light gasoline. When ethanol azeotropic was used, 95 vol% and 50 vol % the maximum volume can be added to react with FCC light gasolines are 15 vol % and 10 vol %, respectively. Because of the fraction of water remaining are not over 0.7 wt %.

6.1.3 Effect of temperature

The etherification reaction is exothermic reaction. To increasing of temperature will be decreasing the ethanol and olefin conversion. Likewise, the result from simulation had been showed the higher conversion at lower temperature than at higher temperature. So, the optimal temperature is 70 ^{o}C. Indeed the catalyst can help isomerization reaction or cracking at high temperature.

6.2 Recommendations

Due to the limitation of ethanol can be added to fuel oil. The procedure of etherification and gasohol are differenced. So, the estimation of cost from gasohol procedures and etherification to produce new reformulate gasoline must be studied in detail. Also, the advantage to environment must be included. If it possible apply the entire FCC gasolines react with ethanol to industry. Total cost, capital cost, operating cost should be considered. Although, today many cars been accepted to use gasohol. Finally, environment impact must be priority to consider.

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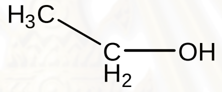
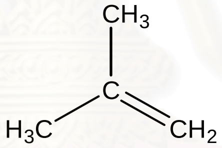
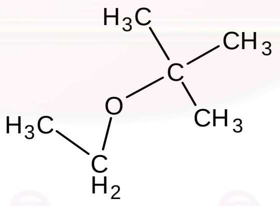
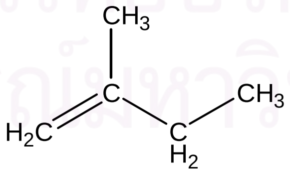
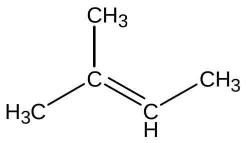
APPENDICES

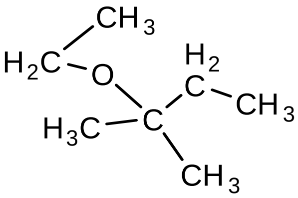
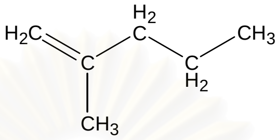
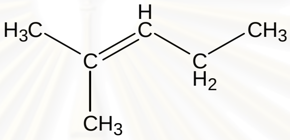
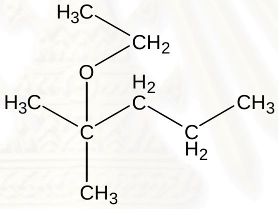
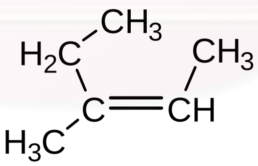
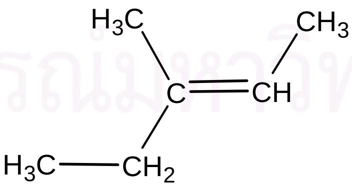
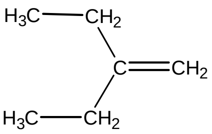
APPENDIX A

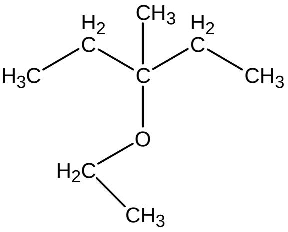
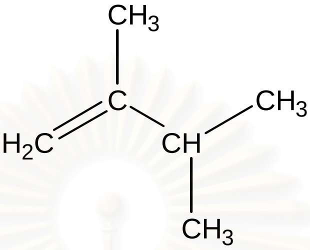
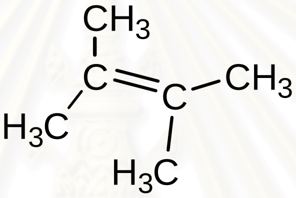
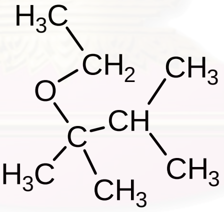
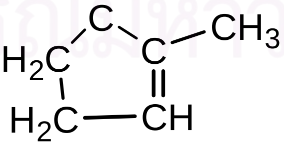
AMBROSE’S GROUP CONTRIBUTION METHOD

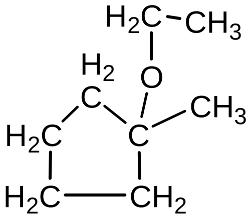
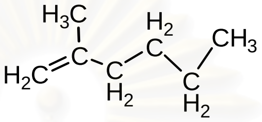
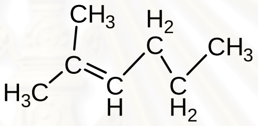
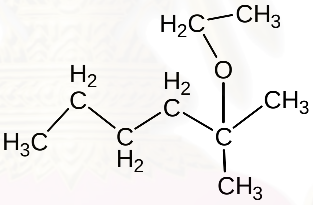
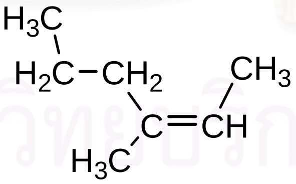
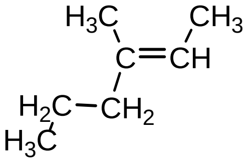
The functional groups of components in olefins are listed below with the number of subgroup in each component. Ambrose’s group contribution method will be used to estimate the property of olefin components. This method can be used to estimate critical properties such as critical temperature and critical pressure.

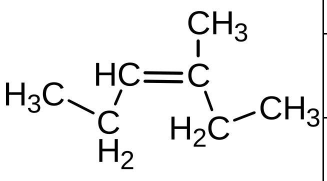
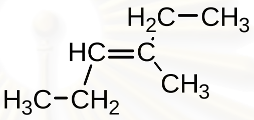
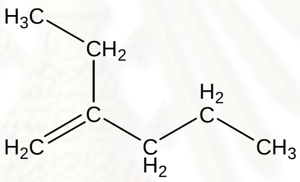
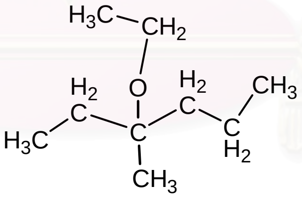
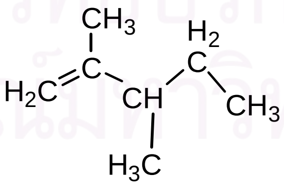
Table A.1 Showed Ambrose’s functional group**.**

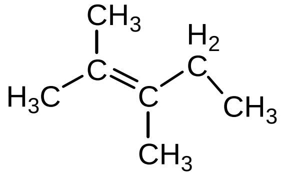
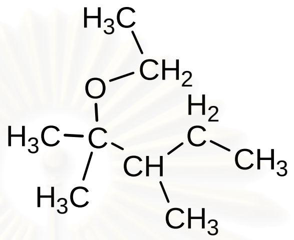
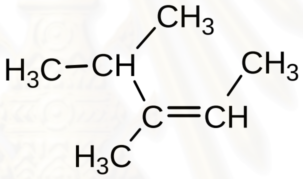
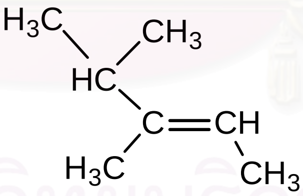
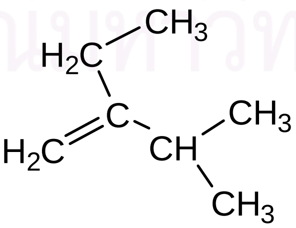
Component/formula	Structure	Type subgroup	No.
Ethanol		Alkyl carbon	2
		-O-	1
isobutene		Alkyl carbon	4
		>C<	1
		Double bond	1
Ethyl-tert-butyl ether		Alkyl carbon	6
		>C<	1
		-O-	1
2-methyl-2-butene		Alkyl carbon	5
		>C<	1
		>CH-	1
		Double bond	1
2-methyl-1-butene		Alkyl carbon	5
		>C<	1
		Double bond	1

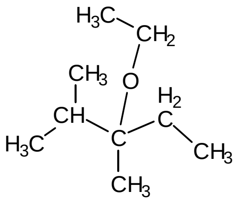
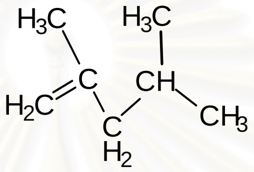
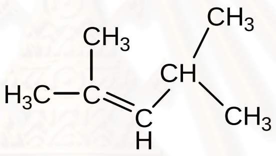
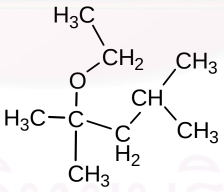
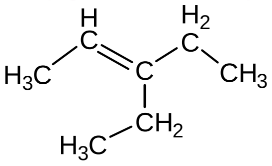
Component/formula	Structure	Type subgroup	No.
2-methyl-2-ethoxybutane		Alkyl carbon	7
		>C<	1
		-O-	1
2-methyl-1-pentene		Alkyl carbon	6
		>C<	1
		Double bond	1
2-methyl-2-pentene		Alkyl carbon	6
		>C<	1
		>CH	1
		Double bond	1
2-methyl-2-ethoxypentane		Alkyl carbon	8
		>C<	1
		-O-	1
cis-3-methyl-2-pentene		Alkyl carbon	6
		>CH-	1
		>C<	1
		Double bond	1
trans-3-methyl-2-pentene		Alkyl carbon	6
		>CH-	1
		>C<	1
		Double bond	1
2-ethyl-1-butene		Alkyl carbon	6
		>C<	1
		Double bond	1

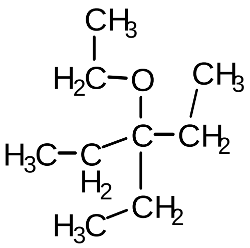
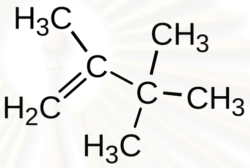
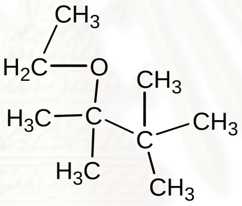
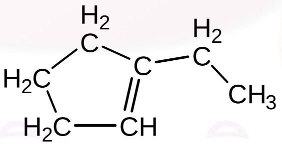
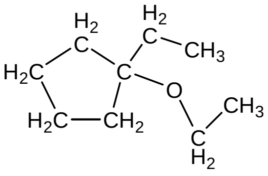
Component/formula	Structure	Type subgroup	No.
3-methyl-3-ethoxypentane		Alkyl carbon	8
		>C<	1
		-O-	1
2,3-dimethyl-1-butene		Alkyl carbon	6
		>CH-	1
		>C<	1
		Double bond	1
2,3-dimethyl-2-butene		Alkyl carbon	6
		>C<	2
		Double bond	1
2,3-dimethyl-2-ethoxybutane		Alkyl carbon	8
		>CH-	1
		>C<	1
		-O-	1
1-methylcyclopentene		Alkyl carbon	6
		-CH2-	3
		>CH-in fuse ring	1
		Ring double bond	1

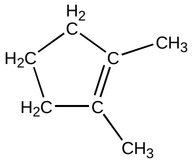
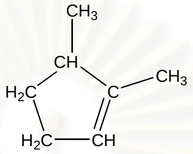
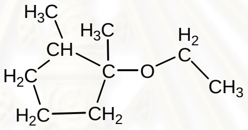
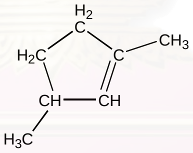
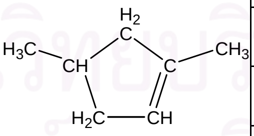
Component/formula	Structure	Type subgroup	No.
1-methyl-1-ethoxycyclopentane		Alkyl carbon	8
		>C<	1
		-CH2- ring	4
		-O-	1
2-methyl-1-hexene		Alkyl carbon	7
		>C<	1
		Double bond	1
2-methyl-2-hexene		Alkyl carbon	2
		>C<	1
		>CH-	1
		Double bond	1
2-methyl-2-ethoxyhexane		Alkyl carbon	9
		>C<	1
		-O-	1
cis-3-methyl-2-hexene		Alkyl carbon	7
		>C<	1
		>CH-	1
		Double bond	1
trans-3-methyl-2-hexene		Alkyl carbon	7
		>C<	1
		>CH-	1
		Double bond	1

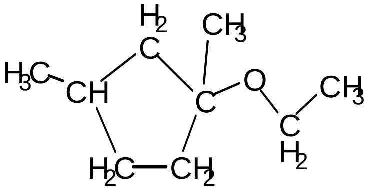
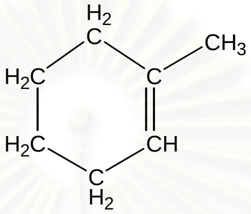
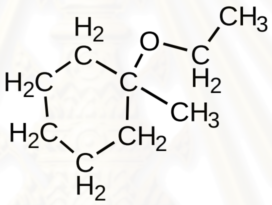
Component/formula	Structure	Type subgroup	No.
cis-3-methyl-3-hexene		Alkyl carbon	7
		>C<	1
		>CH-	1
		Double bond	1
trans-3-methyl-3-hexene		Alkyl carbon	7
		>C<	1
		>CH-	1
		Double bond	1
2-ethyl-1-pentene		Alkyl carbon	7
		>C<	1
		Double bond	1
3-methyl-3-ethoxyhexane		Alkyl carbon	9
		>C<	1
		-O-	1
2,3-dimethyl-1-pentene		Alkyl carbon	7
		>C<	1
		>CH-	1
		Double bond	1

Component/formula	Structure	Type subgroup	No.
2,3-dimethyl-2-pentene		Alkyl carbon	7
		>C<	2
		Double bond	1
2,3-dimethyl-2-ethoxypentane		Alkyl carbon	9
		>CH-	1
		>C<	1
		-O-	1
cis-3,4-dimethyl-2-pentene		Alkyl carbon	7
		>C<	1
		>CH-	2
		Double bond	1
trans-3,4-dimethyl-2-pentene		Alkyl carbon	7
		>C<	1
		>CH-	2
		Double bond	1
2-ethyl-3-methyl-1-butene		Alkyl carbon	7
		>CH-	1
		>C<	1
		Double bond	1

Component/formula	Structure	Type subgroup	No.
2,3-dimethyl-3-ethoxypentane		Alkyl carbon	9
		>CH-	1
		>C<	1
		-O-	1
2,4-dimethyl-1-pentene		Alkyl carbon	7
		>CH-	1
		>C<	1
		Double bond	1
2,4-dimethyl-2-pentene		Alkyl carbon	7
		>CH-	2
		>C<	1
		Double bond	1
2,4-dimethyl-2-ethoxypentane		Alkyl carbon	9
		>C<	1
		>CH-	1
		-O-	1
3-ethyl-2-pentene		Alkyl carbon	7
		>CH-	1
		>C<	1
		Double bond	1

Component/formula	Structure	Type subgroup	No.
3-ethyl-3-ethoxypentane		Alkyl carbon	9
		>C<	1
		-O-	1
2,3,3-trimethyl-1-butene		Alkyl carbon	7
		>C<	2
		Double bond	1
2,3,3-trimethyl-2-ethoxybutane		Alkyl carbon	9
		>C<	2
		-O-	1
1-ethylcyclopentene		Alkyl carbon	7
		>C<	1
		Ring double bond	1
		-CH2- in ring	3
		>CH-in fuse ring	1
1-ethyl-1-ethoxycyclopentane		Alkyl carbon	9
		>C<	1
		-CH2- in ring	4
		-O-	1

Component/formula	Structure	Type subgroup	No.
1,2-dimethylcyclopentene		Alkyl carbon	7
		>C<	2
		-CH2- in ring	3
		Ring double bond	1
1,5-dimethylcyclopentene		Alkyl carbon	7
		>C<	1
		-CH2- in ring	2
		>CH- fuse in ring	2
		Ring double bond	1
1,2-dimethyl-1-ethoxycyclopentane		Alkyl carbon	9
		>C<	1
		-CH2- in ring	3
		>CH-in fuse ring	1
		-O-	1
1,3-dimethylcyclopentene		Alkyl carbon	7
		>C<	1
		-CH2- in ring	2
		>CH- fuse in ring	2
		Ring double bond	1
1,4-dimethylcyclopentene		Alkyl carbon	7
		>C<	1
		-CH2- in ring	2
		>CH- fuse in ring	2
		Ring double bond	1

Component/formula	Structure	Type subgroup	No.
1,3-dimethyl-1-ethoxycyclopentane		Alkyl carbon	9
		>C<	1
		-CH2- in ring	3
		>CH- fuse in ring	1
		-O-	1
1-methylcyclohexene		Alkyl carbon	7
		>C<	1
		-CH2- in ring	5
		>CH- fuse in ring	1
		Ring double bond	1
1-methyl-1-ethoxycyclohexane		Alkyl carbon	9
		>C<	1
		-CH2- in ring	5
		-O-	1

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

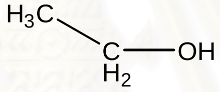
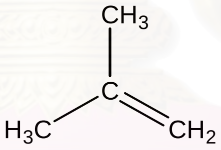
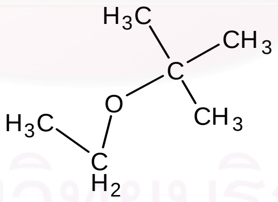
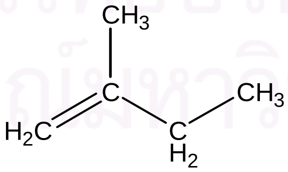
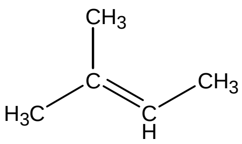
Alkyl group (100), >C< (102), -CH2- fuse in ring (128),
>CH-fuse in ring (129), -O- fuse in ring (131), -O- aliphatic (106),
double bond (103), >CH aliphatic (101), double bond fuse in ring (130).

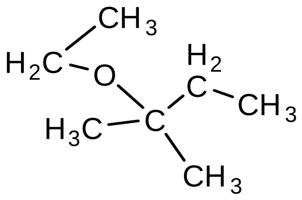
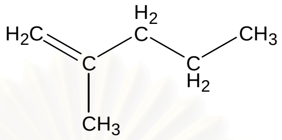
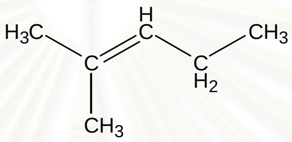
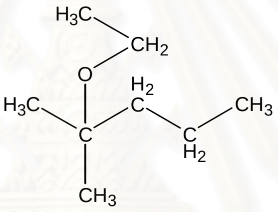
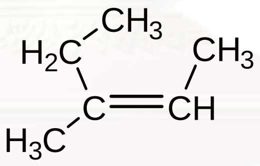
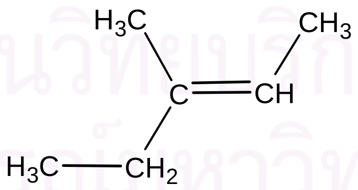
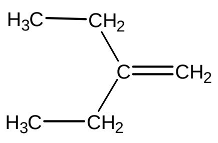
APPENDIX B

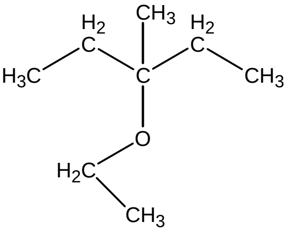
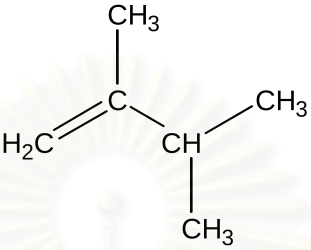
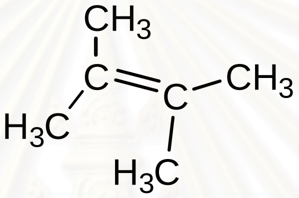
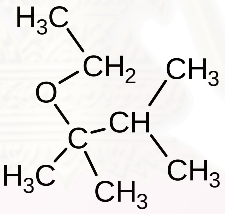
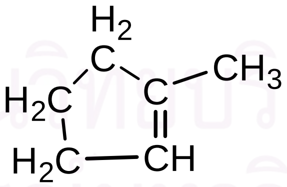
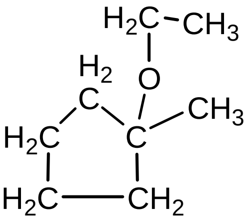
JOBACK’S GROUP CONTRIBUTION METHOD

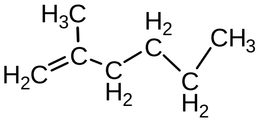
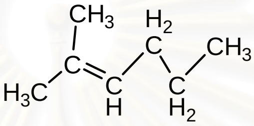
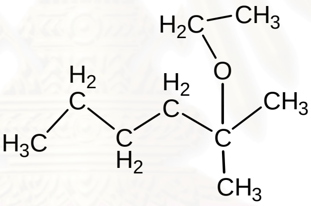
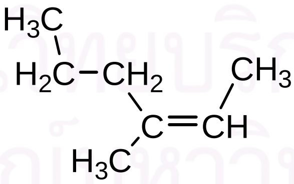
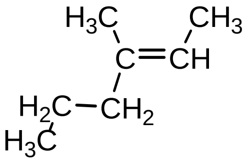
The functional groups of components in olefins are listed below with the number of subgroup in each component. Joback’s group contribution method will be used to estimate the property of olefin components. This method can be used to estimate critical properties such as critical temperature and critical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

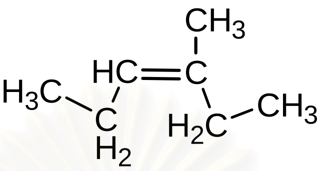
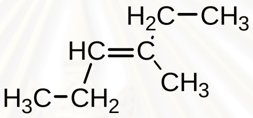
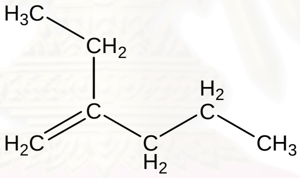
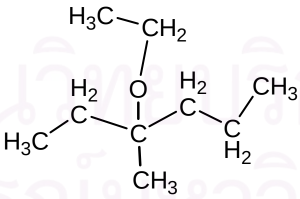
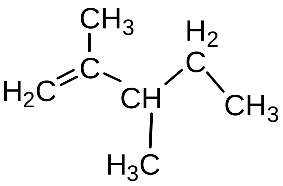
Table B.1 Showed Joback’s subgroup.

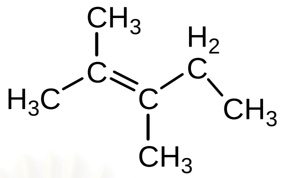
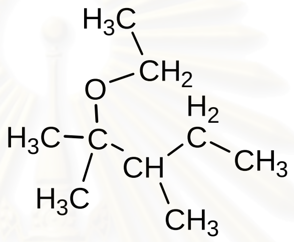
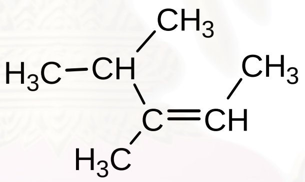
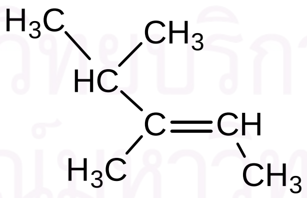
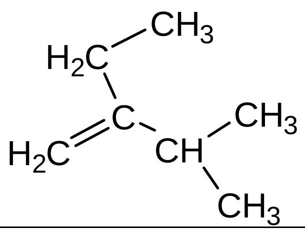
Component/formula	Structure	Type subgroup	No.
Ethanol		CH3(1)	1
		CH2(2)	1
isobutene		CH3(1)	2
		CH2=(1)	1
		C=(3)	1
Ethyl tert-butyl ether		CH3(1)	4
		CH2(2)	1
		C(4)	1
		O(2)	1
2-methyl-2-butene		CH3(1)	3
		C=(3)	1
		CH=(2)	1
2-methyl-1-butene		CH3(1)	2
		CH2(2)	1
		CH2(1)	1
		C=(3)	1

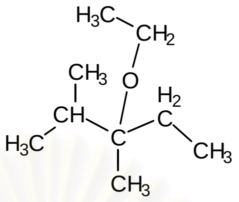
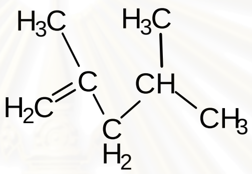
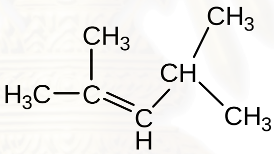
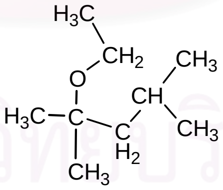
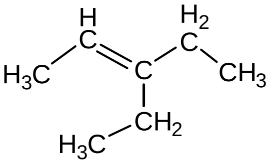
Component/formula	Structure	Type subgroup	No.
2-methyl-2-ethoxybutane		CH3(1)	4
		CH2(2)	2
		C(4)	1
		O(2)	1
2-methyl-1-pentene		CH3(1)	2
		CH2(2)	2
		CH2=(1)	1
		C=(3)	1
2-methyl-2-pentene		CH3(1)	3
		CH2(2)	1
		C=(3)	1
		CH=(2)	1
2-methyl-2-ethoxypentane		CH3(1)	4
		CH2(2)	3
		C(4)	1
		O(2)	1
cis-3-methyl-2-pentene		CH3(1)	3
		CH2(2)	1
		C=(3)	1
		CH=(2)	1
trans-3-methyl-2-pentene		CH3(1)	3
		CH2(2)	1
		C=(3)	1
		CH=(2)	1
2-ethyl-1-butene		CH3(1)	2
		CH2(2)	2
		CH2=(2)	1
		C=(3)	1

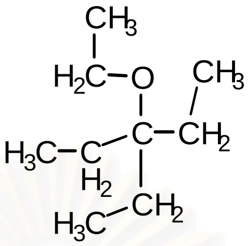
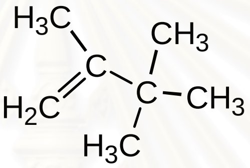
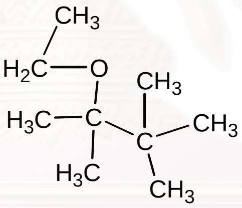
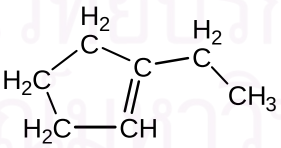
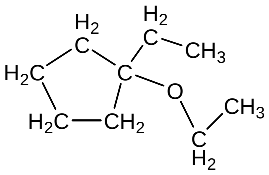
Component/formula	Structure	Type subgroup	No.
3-methyl-3-ethoxypentane		CH3(1)	4
		CH2(2)	3
		C(4)	1
		O(2)	1
2,3-dimethyl-1-butene		CH3(1)	3
		CH(3)	1
		CH2=(1)	1
		C=(3)	1
2,3-dimethyl-2-butene		CH3(1)	4
		C=(3)	2
2,3-dimethyl-2-ethoxybutane		CH3(1)	5
		CH2(2)	1
		C(4)	1
		CH(3)	1
		O(2)	1
1-methylcyclopentene		CH3(1)	1
		CH2	3
		CH=(2)	1
		C=(3)	1
1-methyl-1-ethoxycyclopentane		CH3(1)	2
		CH2	4
		C	1
		CH2(2)	1
		O(2)	1

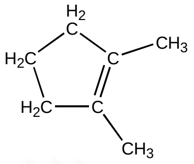
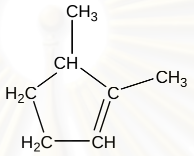
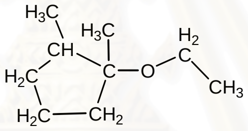
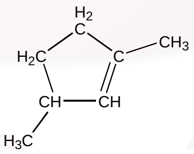
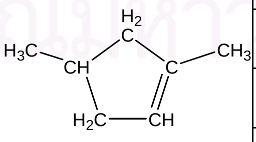
Component/formula	Structure	Type subgroup	No.
2-methyl-1-hexene		CH3(1)	2
		CH2(2)	3
		C=(3)	1
		CH2=(1)	1
2-methyl-2-hexene		CH3(1)	3
		CH2(2)	2
		C=(3)	1
		CH=(2)	1
2-methyl-2-ethoxyhexane		CH3(1)	4
		CH2(2)	4
		C(4)	1
		O(2)	1
cis-3-methyl-2-hexene		CH3(1)	3
		CH2(2)	2
		C=(3)	1
		CH=(2)	1
trans-3-methyl-2-hexene		CH3(1)	3
		CH2(2)	2
		C=(3)	1
		CH=(2)	1

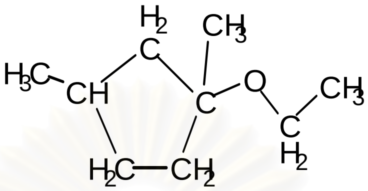
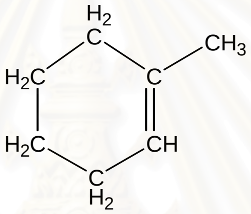
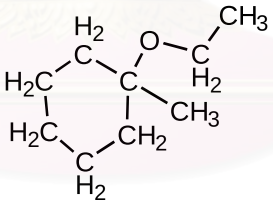
Component/formula	Structure	Type subgroup	No.
cis-3-methyl-3-hexene		CH3(1)	3
		CH2(2)	2
		C=(3)	1
		CH=(2)	1
trans-3-methyl-3-hexene		CH3(1)	3
		CH2(2)	2
		C=(3)	1
		CH=(2)	1
2-ethyl-1-pentene		CH3(1)	2
		CH2(2)	3
		CH2=(1)	1
		C=(3)	1
3-methyl-3-ethoxyhexane		CH3(1)	4
		CH2(2)	4
		C(4)	1
		O(2)	1
2,3-dimethyl-1-pentene		CH3(1)	3
		CH2(2)	1
		CH(3)	1
		CH2=(1)	1
		C=(3)	1

		C=(3)	1
Component/formula	Structure	Type subgroup	No.
2,3-dimethyl-2-pentene		CH3(1)	4
		CH2(2)	1
		C=(3)	1
2,3-dimethyl-2-ethoxypentane		CH3(1)	5
		CH2(2)	2
		C(4)	1
		CH(3)	1
		O(2)	1
cis-3,4-dimethyl-2-pentene		CH3(1)	4
		CH(3)	1
		C=(3)	1
		CH=(2)	1
trans-3,4-dimethyl-2-pentene		CH3(1)	4
		CH(3)	1
		C=(3)	1
		CH=(2)	1
2-ethyl-3-methyl-1-butene		CH3(1)	3
		CH2(2)	1
		CH(3)	1
		CH2=(1)	1

Component/formula	Structure	Type subgroup	No.
2,3-dimethyl-3-ethoxypentane		CH3(1)	5
		CH2(2)	2
		C(4)	1
		CH(3)	1
		O(2)	1
2,4-dimethyl-1-pentene		CH3(1)	3
		CH2(2)	1
		CH(3)	1
		CH2=(1)	1
		C=(3)	1
2,4-dimethyl-2-pentene		CH3(1)	4
		CH(3)	1
		C=(3)	1
		CH=(2)	1
2,4-dimethyl-2-ethoxypentane		CH3(1)	5
		CH2(2)	2
		C(4)	1
		CH(3)	1
		O(2)	1
3-ethyl-2-pentene		CH3(1)	3
		CH2(2)	2
		C=(3)	1
		CH=(2)	1

Component/formula	Structure	Type subgroup	No.
3-ethyl-3-ethoxypentane		CH3(1)	4
		CH2(2)	4
		C(4)	1
		O(2)	1
2,3,3-trimethyl-1-butene		CH3(1)	4
		C(4)	1
		CH2=(1)	1
		C=(3)	1
2,3,3-trimethyl-2-ethoxybutane		CH3(1)	6
		CH2(2)	1
		C(4)	1
		O(2)	1
1-ethylcyclopentene		CH3(1)	1
		CH2	3
		CH=	1
		C=	1
		CH2(2)	1
1-ethyl-1-ethoxycyclopentane		CH3(1)	2
		C	1
		CH2	4
		CH2(2)	2
		O(2)	1

Component/formula	Structure	Type subgroup	No.
1,2-dimethylcyclopentene		CH3(1)	2
		CH2	3
		C=	2
1,5-dimethylcyclopentene		CH3(1)	2
		CH2	2
		CH	1
		CH=	1
		C=	1
1,2-dimethyl-1-ethoxycyclopentane		CH3(1)	3
		CH2	3
		C	1
		CH	1
		CH2(2)	1
		O(2)	1
1,3-dimethylcyclopentene		CH3(1)	2
		CH2	2
		CH	1
		CH=	1
		C=	1
1,4-dimethylcyclopentene		CH3(1)	2
		CH2	2
		CH	1
		C=	1
		CH=	1

Component/formula	Structure	Type subgroup	No.
1,3-dimethyl-1-ethoxycyclopentane		CH3(1)	3
		CH2(2)	2
		C	1
		CH2	3
		CH	1
		O(2)	1
1-methylcyclohexene		CH3(1)	1
		CH2	4
		CH=	1
		C=	1
1-methyl-1-ethoxycyclohexane		CH3(1)	2
		CH2(2)	1
		C	1
		CH2	4
		O(2)	1

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

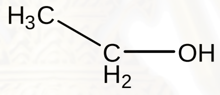
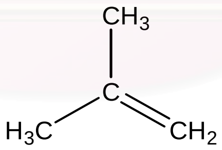
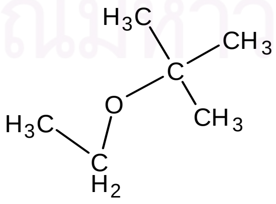
-CH3 (100), >CH2 (101), >CH- (102), >C< (103), =CH2 (104), >CH2 ring increments (110), >CH- ring increment (111), =C< ring increment (114), -O- non-ring (122), -OH alcohols (119).

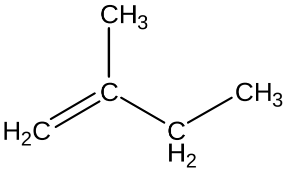
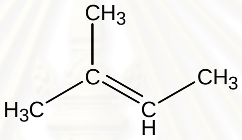
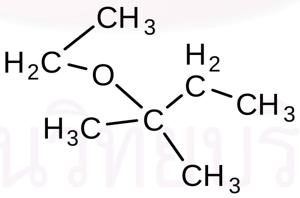
APPENDIX C

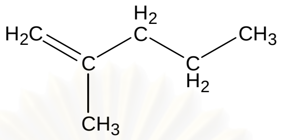
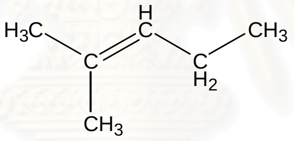
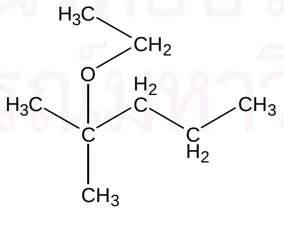
GANI'S GROUP CONTRIBUTION METHOD

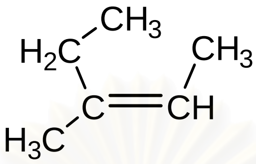
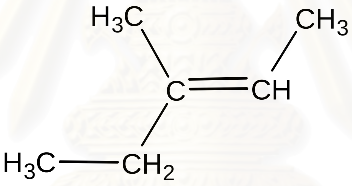
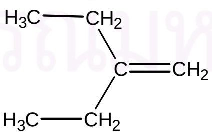
The functional groups of components in olefins are listed below with the number of subgroup in each component. Gani's group contribution method will be used to estimate the property of olefin components. This method can be used to estimate critical properties such as critical temperature and critical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

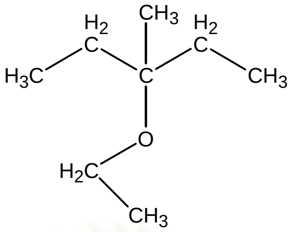
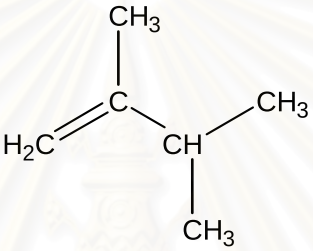
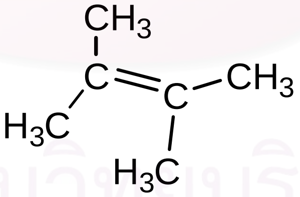
Table C.1 Showed Gani's subgroup**.**

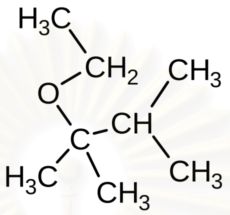
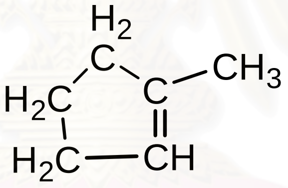
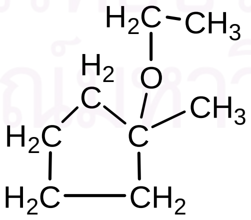
Component/formula	Structure	Type subgroup	No.
Ethanol		CH3	1
		CH2	1
		OH	1
isobutene		First order	
		CH3	2
		CH2=C	1
		Second order	
		CH3-CHm=CHn m,n(0,2)	2
Ethyl tert-butyl ether		First order	
		CH3	4
		C	1
		CH2O	1
		Second order	
		(CH3)3C	1

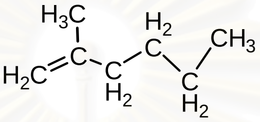
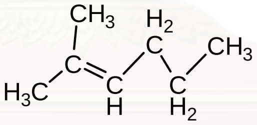
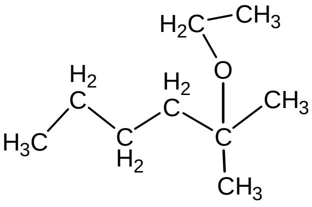
Component/formula	Structure	Type subgroup	No.
2-methyl-2-butene		First order	
		CH3	3
		CH=C	1
		Second order	
		CH3-CHm=CHn m,n(0,2)	3
2-methyl-1-butene		First order	
		CH3	2
		CH2	1
		CH2=C	1
		Second order	
		CH3-CHm=CHn m,n(0,2)	1
		CH2-CHm=CHn m,n(0,2)	1
2-methyl-2-ethoxybutane		First order	
		CH3	4
		CH2	1
		C	1
		CH2O	1

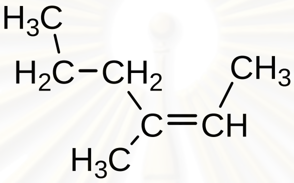
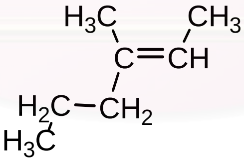
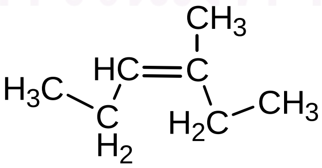
Component/formula	Structure	Type subgroup	No.
2-methyl-1-pentene		First order	
		CH3	2
		CH2	2
		CH2=C	1
		Second order	
		CH3-CHm=CHn m,n(0,2)	1
		CH2-CHm=CHn m,n(0,2)	1
2-methyl-2-pentene		First order	
		CH3	3
		CH2	1
		CH=C	1
		Second order	
		CH3-CHm=CHn m,n(0,2)	2
		CH2-CHm=CHn m,n(0,2)	1
2-methyl-2-ethoxypentane		First order	
		CH3	4
		CH2	2
		C	1
		CH2O	1

Component/formula	Structure	Type subgroup	No.
cis-3-methyl-2-pentene		First order	
		CH3	3
		CH2	1
		CH=C	1
		Second order	
		CH3-CHm=CHn m,n(0,2)	2
		CH2-CHm=CHn m,n(0,2)	1
trans-3-methyl-2-pentene		First order	
		CH3	3
		CH2	1
		CH=C	1
		Second order	
		CH3-CHm=CHn m,n(0,2)	2
		CH2-CHm=CHn m,n(0,2)	1
2-ethyl-1-butene		First order	
		CH3	2
		CH2	2
		CH2=C	1
		Second order	
		CH2-CHm-CHn m,n(0,2)	2

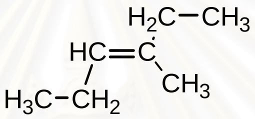
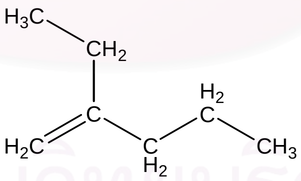
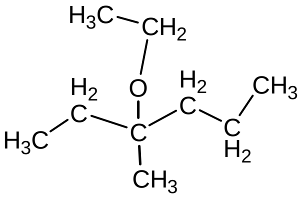
Component/formula	Structure	Type subgroup	No.
3-methyl-3-ethoxypentane		First order	
		CH3	4
		CH2	2
		C	1
		CH2O	1
2,3-dimethyl-1-butene		First order	
		CH3	3
		CH	1
		CH2=C	1
		Second order	
		(CH3)2CH	1
		CH3-CHm=CHn m,n(0,2)	1
		CH-CHm=CHn m,n(0,2)	1
2,3-dimethyl-2-butene		First order	
		CH3	4
		C=C	1
		Second order	
		CH3-CHm=CHn m,n(0,2)	4

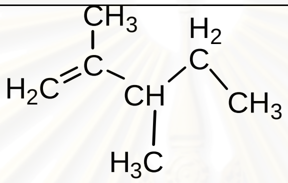
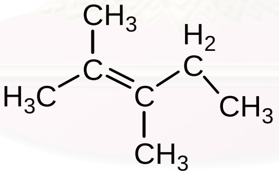
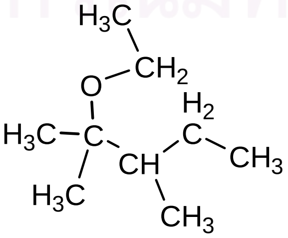
Component/formula	Structure	Type subgroup	No.
2,3-dimethyl-2-ethoxybutane		First order	
		CH3	5
		CH	1
		C	1
		CH2O	1
		Second order	
		(CH3)2CH	1
		CH(CH3)C(CH3)2	1
1-methylcyclopentenet		First order	
		CH3	1
		CH2	3
		CH=C	1
		Second order	
		5 memb. ring	1
1-methyl-1-ethoxycyclopentane		First order	
		CH3	2
		CH2	4
		C	1
		CH2O	1
		Second order	
		5 memb. ring	1

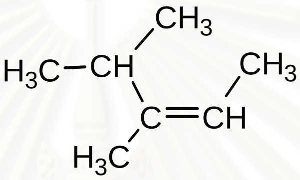
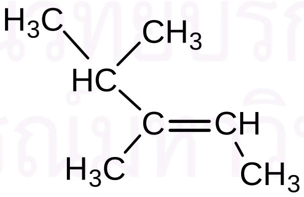
Component/formula	Structure	Type subgroup	No.
2-methyl-1-hexene		First order	
		CH3	2
		CH2	3
		CH2=C	1
		Second order	
		CH3-CHm=CHn m,n(0,2)	1
2-methyl-2-hexene		First order	
		CH3	3
		CH2	2
		CH=C	1
		Second order	
		CH3-CHm=CHn m,n(0,2)	2
		CH2-CHm=CHn m,n(0,2)	1
2-methyl-2-ethoxyhexane		First order	
		CH3	4
		CH2	3
		C	1
		CH2O	1

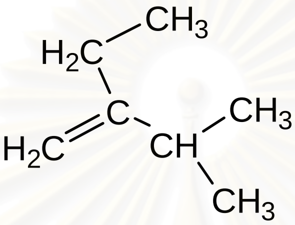
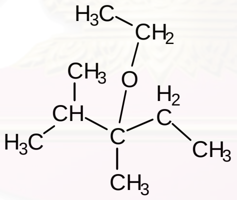
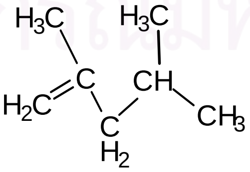
Component/formula	Structure	Type subgroup	No.
cis-3-methyl-2-hexene		First order	
		CH3	3
		CH2	2
		CH=C	1
		Second order	
		CH3=CHm=CHn m,n(0,2)	2
		CH2-CHm=CHn m,n(0,2)	1
trans-3-methyl-2-hexene		First order	
		CH3	3
		CH2	2
		CH=C	1
		Second order	
		CH3=CHm=CHn m,n(0,2)	2
		CH2-CHm=CHn m,n(0,2)	1
cis-3-methyl-3-hexene		First order	
		CH3	3
		CH2	2
		CH=C	1
		Second order	
		CH3=CHm=CHn	1

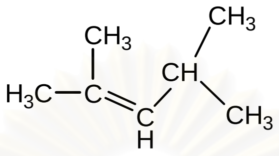
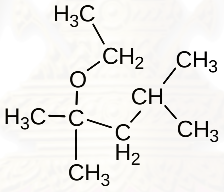
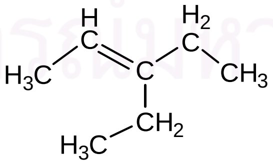
		m,n(0,2)	
		CH2-CHm=CHn m,n(0,2)	2

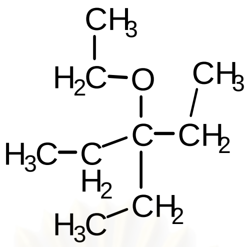
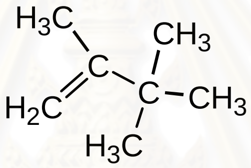
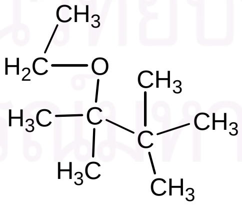
		CH2O	1
Component/formula	Structure	Type subgroup	No.
trans-3-methyl-3-hexene		First order	
		CH3	3
		CH2	2
		CH=C	1
		Second order	
		CH3=CHm=CHn m,n(0,2)	1
		CH2-CHm=CHn m,n(0,2)	2
2-ethyl-1-pentene		First order	
		CH3	2
		CH2	3
		CH2=C	1
		Second order	
		CH2-CHm=CHn m,n(0,2)	2
3-methyl-3-ethoxyhexane		First order	
		CH3	4
		CH2	3
		C	1

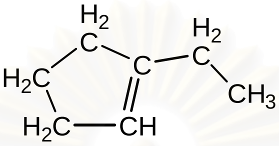
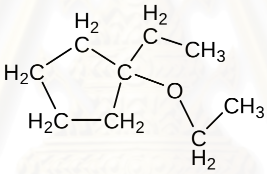
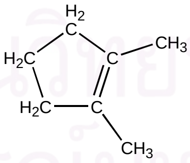
		CH2O	1
Component/formula	Structure	Type subgroup	No.
		Second order First order	
		CH3 CH(CH3)C(CH3)2	3 1
		CH2	1
2,3-dimethyl-1-pentene		CH	1
		CH2=C	1
		Second order	
		CH3-CHm=CHn m,n(0,2)	1
		CH-CHm=CHn m,n(0,2)	1
2,3-dimethyl-2-pentene		First order	
		CH3	4
		CH2	1
		C=C	1
		Second order	
		CH3-CHm=CHn m,n(0,2)	3
		CH2-CHm=CHn m,n(0,2)	1
2,3-dimethyl-2-ethoxypentane		First order	
		CH3	5
		CH2	1
		CH	1
		C	1

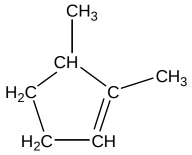
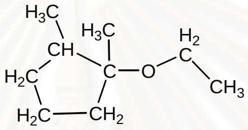
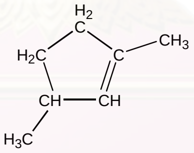
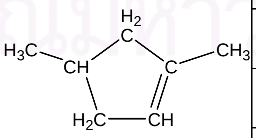
Component/formula	Structure	Type subgroup	No.
cis-3,4-dimethyl-2-pentene		First order	
		CH3	4
		CH	1
		CH=C	1
		Second order	
		(CH3)2CH	1
		CH3-CHm=CHn m,n(0,2)	2
		CH-CHm=CHn m,n(0,2)	1
trans-3,4-dimethyl-2-pentene		First order	
		CH3	4
		CH	1
		CH=C	1
		Second order	
		(CH3)2CH	1
		CH3-CHm=CHn m,n(0,2)	2
		CH-CHm=CHn m,n(0,2)	1

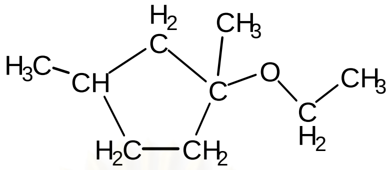
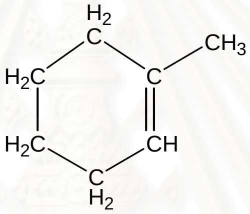
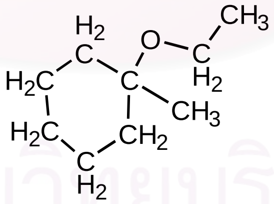
		CH3-CHm=CHn m,n(0,2)	1
Component/formula	Structure	Type subgroup	No.
		CH2-CHm=CHn m,n(0,2) First order	1
2-ethyl-3-methyl-1-butene		CH3	3
		CH2	1
		CH	1
		CH2=C	1
		Second order	
		(CH3)2CH	1
		CH2-CHm=CHn m,n(0,2)	1
		CH-CHm=CHn m,n(0,2)	1
2,3-dimethyl-3-ethoxypentane		First order	
		CH3	5
		CH2	1
		CH	1
		C	1
		CH2O	1
		Second order	
		(CH3)2CH	1
2,4-dimethyl-1-pentene		First order	
		CH3	3
		CH2	1
		CH	1
		CH2=C	1
		Second order	
		(CH3)2CH	1

Component/formula	Structure	Type subgroup	No.
2,4-dimethyl-2-pentene		First order	
		CH3	4
		CH	1
		CH=C	1
		Second order	
		(CH3)2CH	1
		CH3-CHm-CHn m,n(0,2)	2
		CH-CHm=CHn m,n(0,2)	1
2,4-dimethyl-2-ethoxypentane		First order	
		CH3	5
		CH2	1
		CH	1
		C	1
		CH2O	1
		Second order	
		(CH3)2CH	1
3-ethyl-2-pentene		First order	
		CH3	3
		CH2	2
		CH=C	1
		Second order	
		CH3-CHm=CHn m,n(0,2)	1
		CH2-CHm=CHn m,n(0,2)	2

Component/formula	Structure	Type subgroup	No.
3-ethyl-3-ethoxypentane		First order	
		CH3	4
		CH2	3
		C	1
		CH2O	1
2,3,3-trimethyl-1-butene		First order	
		CH3	4
		C	1
		CH2=C	1
		Second order	
		(CH3)3C	1
		CH3-CHm=CHn m,n(0,2)	1
		CH-CHm=CHn m,n(0,2)	1
2,3,3-trimethyl-2-ethoxybutane		First order	
		CH3	6
		C	2
		CH2O	1
		Second order	
		(CH3)3C	1
		C(CH3)2C(CH3)2	1

Component/formula	Structure	Type subgroup	No.
1-ethylcyclopentene	 	First order	
		CH3	1
		CH2	4
		CH=C	1
		Second order	
		5 memb. ring	1
1-ethyl-1-ethoxycyclopentane	 	First order	
		CH3	2
		CH2	5
		C	1
		CH2O	1
		Second order	
		5 memb. ring	1
1,2-dimethylcyclopentene	 	First order	
		CH3	2
		CH2	3
		C=C	1
		Second order	
		5 memb. ring	1

Component/formula	Structure	Type subgroup	No.
1,5-dimethylcyclopentene		First order	
		CH3	2
		CH2	2
		CH	1
		CH=C	1
		Second order	
		5 memb. ring	1
1,2-dimethyl-1-ethoxycyclopentane		First order	
		CH3	3
		CH2	3
		CH	1
		C	1
		CH2O	1
		Second ring	
		5 memb. ring	1
1,3-dimethylcyclopentene		First order	
		CH3	2
		CH2	2
		CH	1
		CH=C	1
		Second order	
		5 menb. ring	1
1,4-dimethylcyclopentene		First order	
		CH3	2
		CH2	2
		CH	1
		CH=C	1
		Second order	
		Memb. ring	1

Component/formula	Structure	Type subgroup	No.
1,3-dimethyl-1-ethoxycyclopentane		First order	
		CH3	3
		CH2	3
		CH	1
		C	1
		CH2O	1
		Second order	
		5 memb. ring	1
1-methylcyclohexene		First order	
		CH3	1
		CH2	4
		CH=C	1
		Second order	
		6 memb.ring	
1-methyl-1-ethoxycyclohexane		First order	
		CH3	2
		CH2	5
		C	1
		CH2O	1
		Second order	
		6 memb. ring	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).

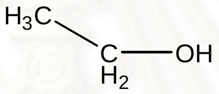
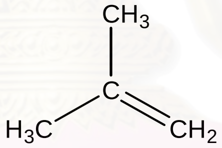
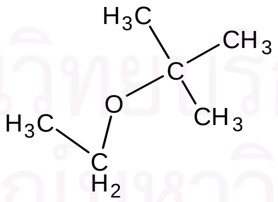
Second order; (CH3)2CH- (5000), -C(CH3)2C(CH3)2- (5020), CH3-C=CH2 (5175), CH2-C=CH2 (5205), CH-C=CH2 (5235), 5-member ring correction (5035), 6-member ring correction (5040),

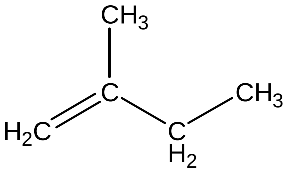
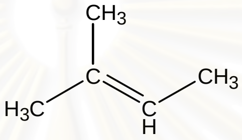
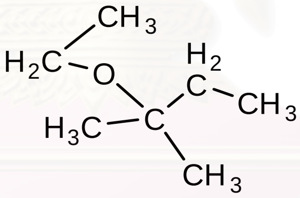
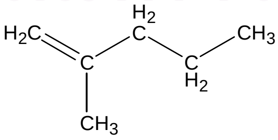
APPENDIX D

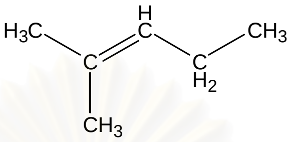
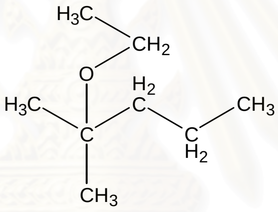
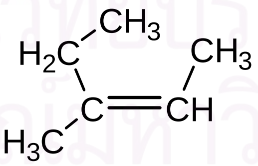
BENSON’S GROUP CONTRIBUTION METHOD

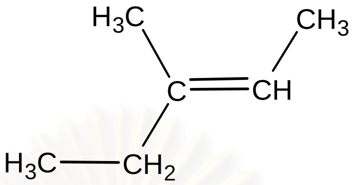
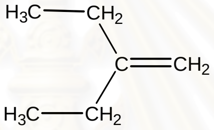
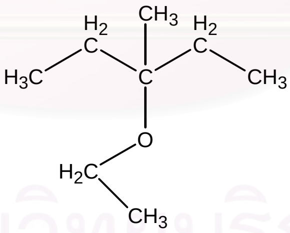
The functional groups of components in olefins are listed below with the number of subgroup in each component. Benson’s group contribution method is used to estimate the property of olefin components. This method will be used to estimate thermodynamic properties, Gibbs of formation.

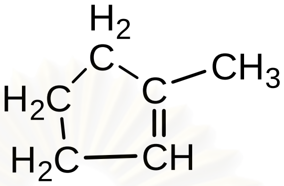
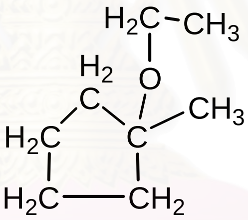
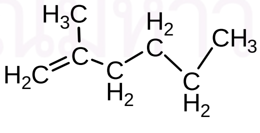
Table D.1 Showed Benson’s subgroup.

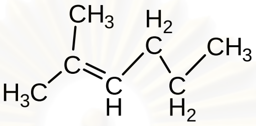
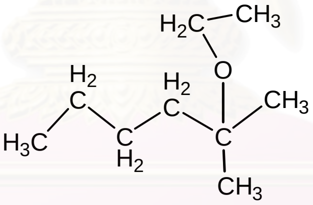
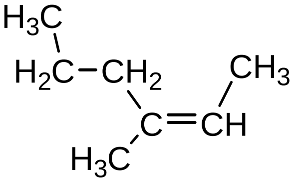
Component/formula	Structure	Type subgroup	No.
Ethanol		CH3-(C)	1
		CH2-(2C)	1
		OH	1
isobutene		CH3—(C=)	2
		CH2=	1
		=C-(2C)	1
		Optical isomer	1
		Total symmetry	2
Ethyl tert-butyl ether		CH3-(C)	4
		CH2-(C,O)	1
		C-(3C,O)	1
		O-(2C)	1
		Gauche O	1
		Optical isomer	1
		Total symmetry	3

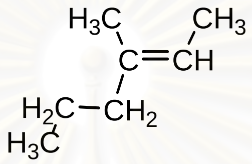
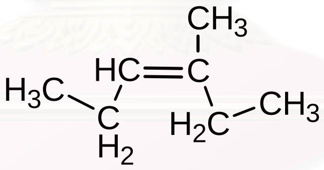
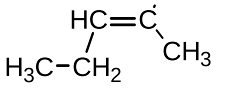
Component/formula	Structure	Type subgroup	No.
2-methyl-2-butene		CH3-(=C)	3
		=C-(2C)	1
		=CH-(C)	1
		Cis-	1
		Optical isomer	1
		Total symmetry	1
2-methyl-1-butene		CH3-(C)	1
		CH3-(C=)	1
		CH2=	1
		=C-(2C)	2
		CH2-(C,=C)	1
		Optical isomer	1
		Total symmetry	1
2-methyl-2-ethoxybutane		CH3-(C)	4
		CH2-(2C)	1
		CH2-(C,O)	1
		C-(3C,O)	1
		O-(2C)	1
		Gauche O	1
		Gauche C	1
		Optical isomer	1
		Total symmetry	1
2-methyl-1-pentene		CH3-(C)	1
		CH2-(2C)	1
		CH3-(=C)	1
		CH2 =	1
		= C-(2C)	1
		CH2-(C,=C)	1
		Optical isomer	1
		Total symmetry	1

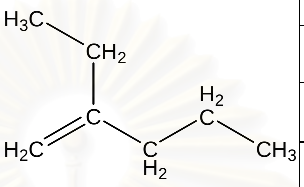
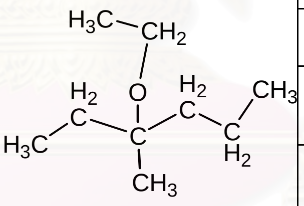
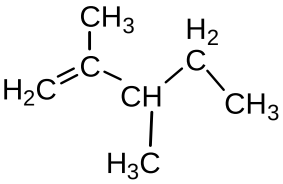
Component/formula	Structure	Type subgroup	No.
2-methyl-2-pentene		CH3-(C)	1
		CH3-(=C)	2
		= C-(2C)	1
		= CH - (C)	1
		CH2-(C,=C)	1
		Cis-	1
		Optical isomer	1
		Total symmetry	1
2-methyl-2-ethoxypentane		CH3-(C)	4
		CH2-(2C)	2
		CH2-(C,O)	1
		C-(3C,O)	1
		O-(2C)	1
		Gauche O	1
		Gauche C	1
		Optical isomer	1
		Total symmetry	1
cis-3-methyl-2-pentene		CH3-(C)	1
		CH3-(=C)	2
		=C-(2C)	1
		=CH-(C)	1
		CH2-(C,=C)	1
		Cis-	1
		Optical isomer	1
		Total symmetry	1

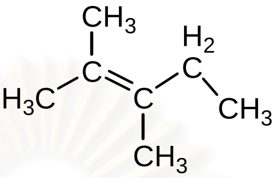
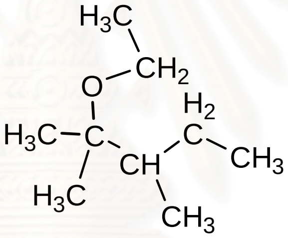
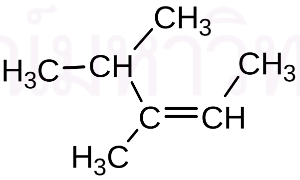
Component/formula	Structure	Type subgroup	No.
trans-3-methyl-2-pentene		CH3-(C)	1
		CH3-(=C)	2
		=C-(2C)	1
		=CH-(C)	1
		CH2-(C,=C)	1
		Optical isomer	1
		Total symmetry	1
2-ethyl-1-butene		CH3-(C)	2
		CH2=	1
		=C-(2C)	1
		CH2-(C,=C)	2
		Optical isomer	1
		Total symmetry	2
3-methyl-3-ethoxypentane		CH3-(C)	4
		CH2-(2C)	2
		CH2-(C,O)	1
		C-(3C,O)	1
		O-(2C)	1
		Gauche O	1
		Gauche C	2
		Optical isomer	1
		Total symmetry	1

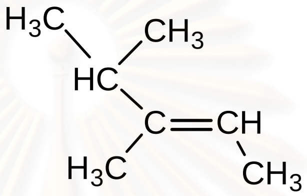
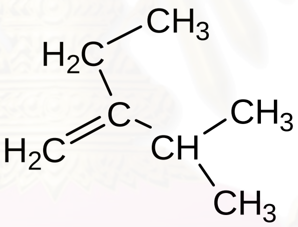
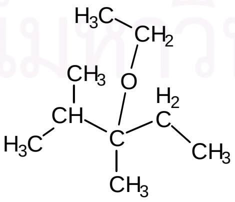
Component/formula	Structure	Type subgroup	No.
1-methylcyclopentene		CH2-(2C)	1
		CH3-(=C)	1
		=C-(2C)	1
		=CH-(C)	1
		CH2-(C,=C)	2
		Cyclopentene	1
		Optical isomer	1
		Total symmetry	1
1-methyl-1-ethoxycyclopentane		CH3-(C)	2
		CH2-(2C)	4
		CH2-(C,O)	1
		C,(3C,O)	1
		O-(2C)	1
		Cyclopentane	1
		Optical isomer	1
		Total symmetry	1
2-methyl-1-hexene		CH3-(C)	1
		CH2-(2C)	2
		CH3-(=C)	1
		CH2=	1
		=C-(2C)	1
		CH2-(C,=C)	1
		Optical isomer	1
		Total symmetry	1

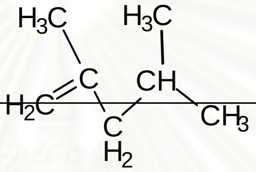
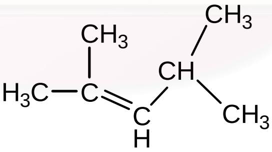
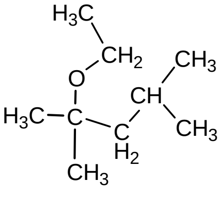
Component/formula	Structure	Type subgroup	No.
2-methyl-2-hexene		CH3-(C)	1
		CH2-(2C)	2
		CH3-(=C)	1
		CH2=	1
		=C-(2C)	1
		CH2-(C,=C)	1
		Optical isomer	1
		Total symmetry	1
2-methyl-2-ethoxyhexane		CH3-(C)	4
		CH2-(2C)	3
		CH2-(C,O)	1
		C(3C,O)	1
		O-(2C)	1
		Gauche O	1
		Gauche C	1
		Optical isomer	1
		Total symmetry	1
cis-3-methyl-2-hexene		CH3-(C)	1
		CH2-(2C)	1
		CH3-(=C)	2
		=C-(2C)	1
		=CH-(C)	1
		CH2-(C,=C)	1
		Cis-	1
		Optical	1
		Total symmetry	1

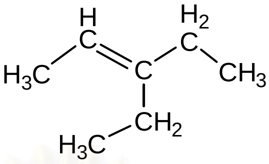
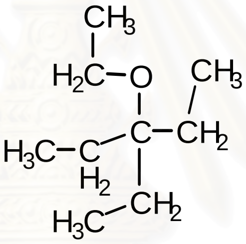
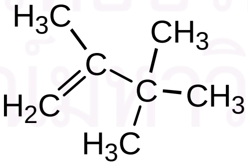
Component/formula	Structure	Type subgroup	No.
trans-3-methyl-2-hexene		CH3-(C)	1
		CH2-(2C)	1
		CH3-(=C)	2
		=C-(2C)	1
		=CH-(C)	1
		CH2-(C,=C)	1
		Optical	1
		Total symmetry	1
cis-3-methyl-3-hexene		CH3-(C)	2
		CH3(=C)	1
		=C-(2C)	1
		=CH-(C)	1
		CH2-(C,=C)	2
		Cis-	1
		Optical isomer	1
		Total symmetry	1
trans-3-methyl-3-hexene		CH3-(C)	2
		CH3(=C)	1
		=C-(2C)	1
		=CH-(C)	1
		CH2-(C,=C)	2
		Optical isomer	1
		Total symmetry	1

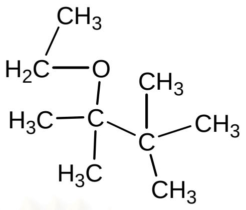
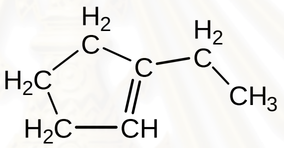
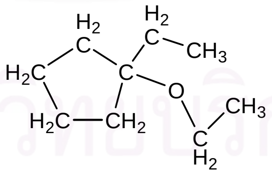
		Optical isomer	2
Component/formula	Structure	Type subgroup	No.
		Total symmetry	1
		CH3-(C)	2
2-ethyl-1-pentene		CH2-(2C)	1
		CH2=	1
		=C-(2C)	1
		CH2-(C,=C)	2
		Optical isomer	1
		Total symmetry	1
3-methyl-3-ethoxyhexane		CH3-(C)	4
		CH2-(2C)	3
		CH2-(C,O)	1
		C-(3C,O)	1
		O-(2C)	1
		Gauche O	1
		Gauche C	2
		Optical isomer	2
		Total symmetry	1
2,3-dimethyl-1-pentene		CH3-(C)	2
		CH2-(2C)	1
		CH3-(=C)	1
		CH2=	1
		=C-(C)	1
		CH-(2C,=C)	1

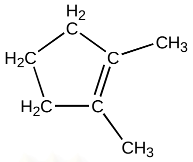
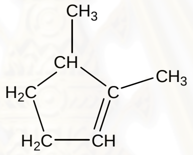
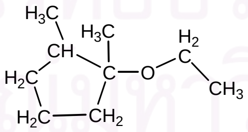
Component/formula	Structure	Type subgroup	No.
2,3-dimethyl-2-pentene		CH3-(C)	1
		CH3-(=C)	3
		=C-(2C)	2
		CH2-(2C,=C)	1
		Cis-	2
		Optical isomer	1
		Total symmetry	1
2,3-dimethyl-2-ethoxypentane		CH3-(C)	5
		CH2-(2C)	1
		CH-(3C)	1
		CH2-(C,O)	1
		C-(3C,O)	1
		O-(2C)	1
		Gauche O	1
		Gauche C	3
		Optical isomer	2
		Total symmetry	1
cis-3,4-dimethyl-2-pentene		CH3-(C)	2
		CH3-(=C)	2
		=C-(2C)	2
		=C-(2C)	1
		=CH-(C)	1
		CH-(2C,=C)	1
		Cis-	1
		Optical isomer	1
		Total symmetry	1

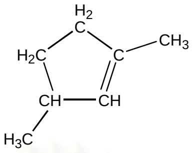
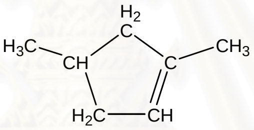
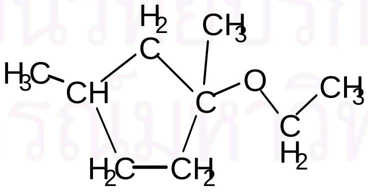
Component/formula	Structure	Type subgroup	No.
trans-3,4-dimethyl-2-pentene		CH3-(C)	2
		CH3-(=C)	2
		=C-(2C)	2
		=C-(2C)	1
		=CH-(C)	1
		CH-(2C,=C)	1
		Optical isomer	1
		Total symmetry	1
2-ethyl-3-methyl-1-butene		CH3-(C)	3
		CH2=	1
		=C-(2C)	1
		CH2-(C,=C)	1
		CH-(2C,=C)	1
		Optical isomer	1
		Total symmetry	1
2,3-dimethyl-3-ethoxypentane		CH3-(C)	5
		CH2-(2C)	1
		CH-(3C)	1
		CH2-(C,O)	1
		C-(3C,O)	1
		O-(2C)	1
		Gauche O	1
		Gauche C	3
		Optical isomer	2
		Total symmetry	1

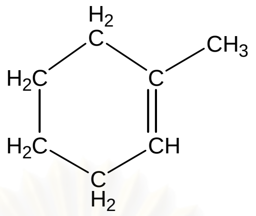
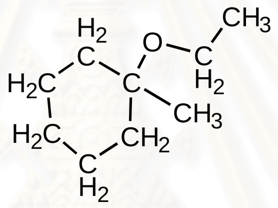
Component/formula	Structure	Type subgroup	No.
		O-(2C)	1
2,4-dimethyl-1-pentene		CH3-(C) Gauche (C)	2 1
		CH3-(=C) Gauche (C)	1 2
		CH2= Optical isomer	1 1
		=C-(2C) Total symmetry	1 1
		CH2-(C,=C)	1
		CH-(3C)	1
		Optical isomer	1
		Total symmetry	1
2,4-dimethyl-2-pentene		CH3-(C)	2
		CH3-(=C)	2
		=C-(2C)	1
		=CH-(C)	1
		CH-(2C,=C)	1
		Cis-	1
		Optical isomer	1
		Total symmetry	1
2,4-dimethyl-2-ethoxypentane		CH3-(C)	5
		CH2-(2C)	1
		CH-(3C)	1
		CH2-(C,O)	1
		C-(3C,O)	1

Component/formula	Structure	Type subgroup	No.
3-ethyl-2-pentene		CH3-(C)	2
		CH2-(=C)	1
		=C-(2C)	1
		=CH-(C)	1
		CH2-(C,=C)	2
		Cis-	1
		Optical isomer	1
		Total symmetry	1
3-ethyl-3-ethoxypentane		CH3-(C)	4
		CH2-(2C)	3
		CH2-(C,O)	1
		C-(3C,O)	1
		O-(2C)	1
		Gauche O	1
		Gauche C	3
		Optical isomer	1
		Total symmetry	3
2,3,3-trimethyl-1-butene		CH3-(C)	3
		CH3-(=C)	1
		CH2=	1
		=C-(2C)	1
		C-(3C,=C)	1
		Optical isomer	1
		Total symmetry	3

Component/formula	Structure	Type subgroup	No.
2,3,3-trimethyl-2-ethoxybutane		CH3-(C)	6
		C-(4C)	1
		CH2-(C,O)	1
		C-(3C,O)	1
		O-(2C)	1
		Gauche O	1
		Gauche C	4
		Optical isomer	1
		Total symmetry	3
1-ethylcyclopentene		CH3-(C)	1
		CH2-(2C)	1
		=C-(2C)	1
		=CH-(C)	1
		CH2-(C,=C)	3
		Cyclopentene	1
		Optical isomer	1
		Total symmetry	1
1-ethyl-1-ethoxycyclopentane		CH3-(C)	2
		CH2-(2C)	5
		CH2-(C,O)	1
		C-(3C,O)	1
		O-(2C)	1
		Cyclopentane	1
		Gauche C	1
		Optical isomer	1
		Total symmetry	1

Component/formula	Structure	Type subgroup	No.
1,2-dimethylcyclopentene		CH2-(2C)	1
		CH3-(=C)	2
		=C-(2C)	2
		CH2-(C,=C)	2
		Cyclopentene	1
		Optical isomer	1
		Total symmetry	2
1,5-dimethylcyclopentene		CH3-(C)	1
		CH2-(2C)	1
		CH3-(=C)	1
		=C-(2C)	1
		=CH-(C)	1
		CH2-(C,=C)	1
		CH-(2C,=C)	1
		Cyclopentene	1
		Optical isomer	2
		Total symmetry	1
1,2-dimethyl-1-ethoxycyclopentane		CH3-(C)	3
		CH2-(2C)	3
		CH-(3C)	1
		CH2-(C,O)	1
		C-(3C,O)	1
		O-(2C)	1
		Cyclopentane	1
		Gauche C	1
		Optical isomer	1
		Total symmetry	1

Component/formula	Structure	Type subgroup	No.
1,3-dimethylcyclopentene		CH3-(C)	1
		CH2-(2C)	1
		CH3-(=C)	1
		=C-(2C)	1
		=CH-(C)	1
		CH2-(C,=C)	1
		CH-(2C,=C)	1
		Cyclopentene	1
		Optical isomer	2
1,4-dimethylcyclopentene		Total symmetry	1
		CH3-(C)	1
		CH3(=C)	1
		=C-(2C)	1
		=CH-(C)	1
		CH2-(C,=C)	2
		CH-(3C)	1
		Cyclopentene	1
		Optical isomer	2
		Total symmetry	1
1,3-dimethyl-1-ethoxycyclopentane		CH3-(C)	3
		CH2-(2C)	3
		CH-(3C)	1
		CH2-(C,O)	1
		C-(3C,O)	1
		O-(2C)	1
		Cyclopentane	1
		Optical isomer	2
		Total symmetry	1

Component/formula	Structure	Type subgroup	No.
1-methylcyclohexene		CH2-(2C)	2
		CH3-(=C)	1
		=C-(2C)	1
		=CH-(C)	1
		CH2-(C,=C)	2
		Cyclohexene	1
		Optical isomer	1
		Total symmetry	1
1-methyl-1-ethoxycyclohexane		CH3-(C)	2
		CH2-(2C)	5
		CH2-(C,O)	1
		C-(3C,O)	1
		O-(2C)	1
		Cyclohexane	1
		Optical isomer	1
		Total symmetry	1

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) symmetry (405)
optical isomers (406)

APPENDIX E

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;

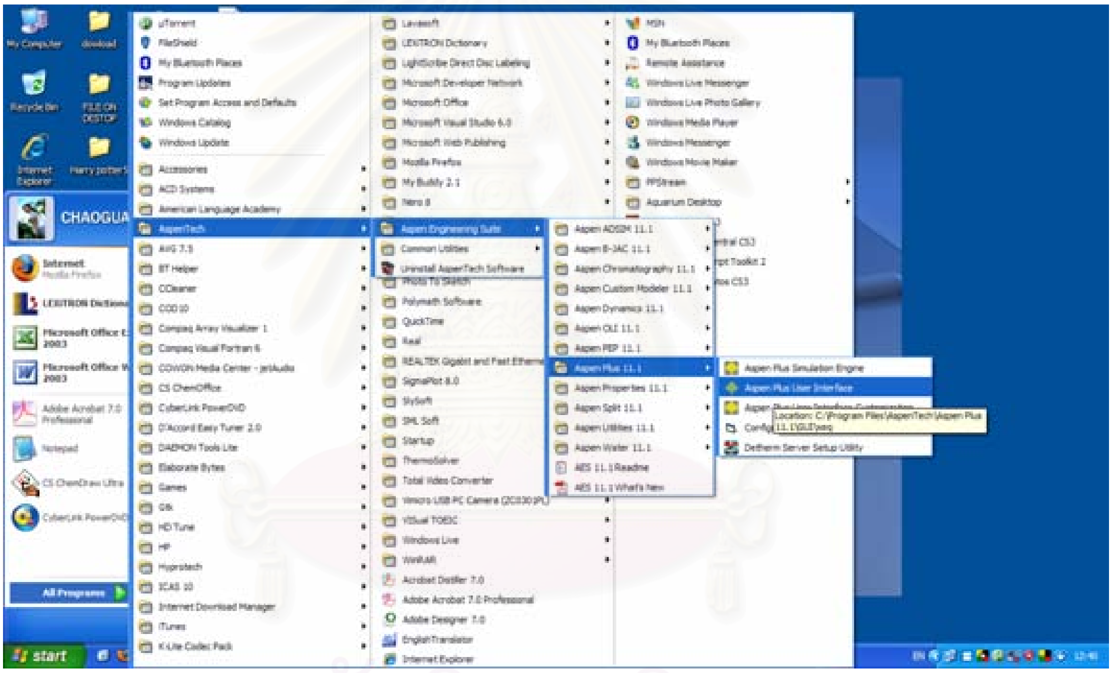


Figure E-1 Open the Aspen plus program.

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.

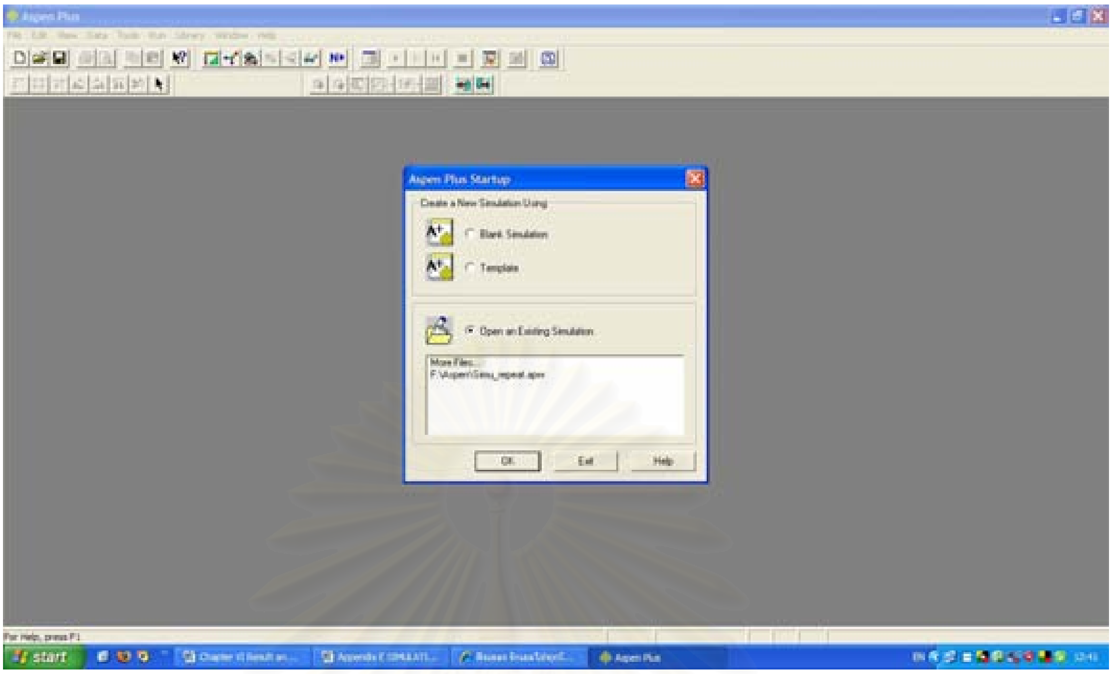


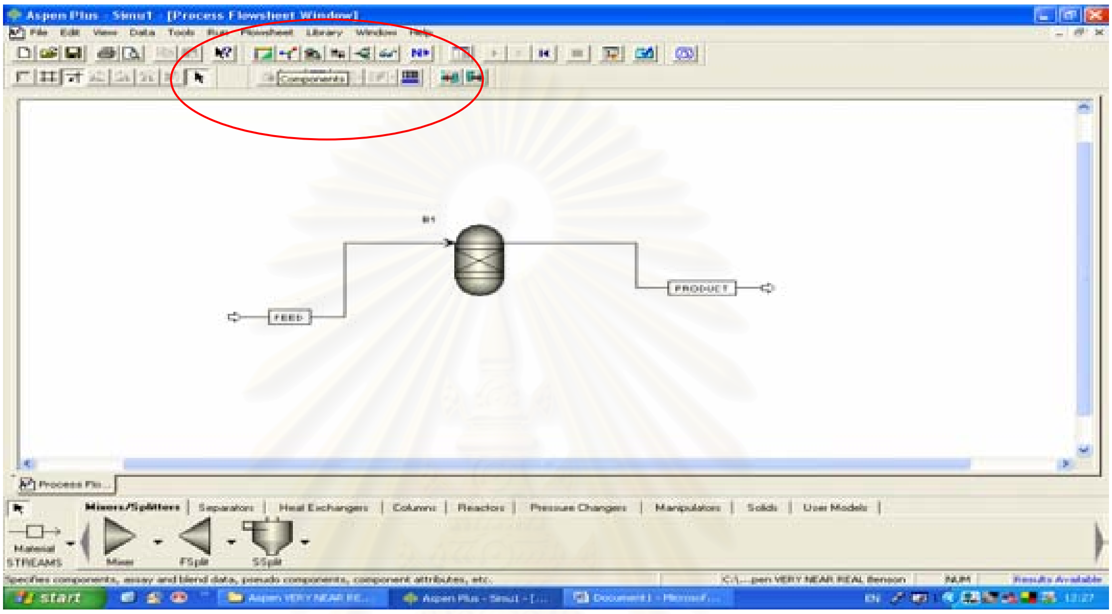
Figure E-2 Choose type of open the Aspen plus program.

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.

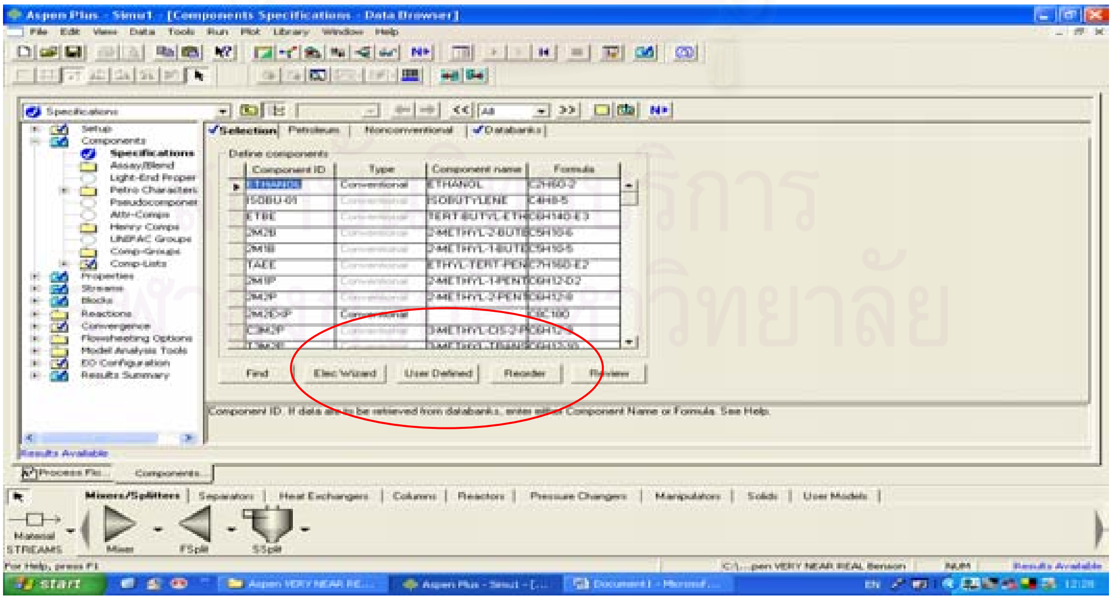
The procedures of using Aspen plus to simulate follow this research. To explanations the step by step to add the new components to Aspen plus program databank are listed below.



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.

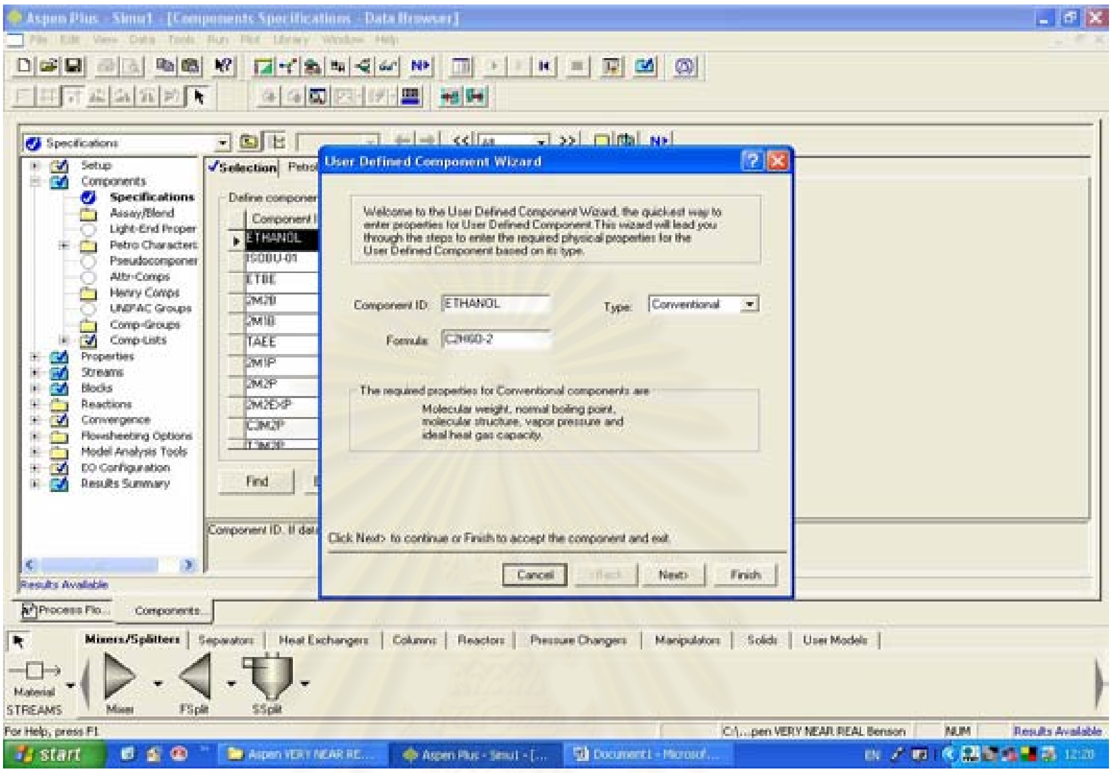


Component ID	Type	Component name	Formula
ETHANOL	Conventional	ETHANOL	C2H6O-2
ISOBU-01	Conventional	ISOBUTYLENE	C4H8-5
ETBE	Conventional	TERT-BUTYL-ETH	C6H14O-E3
2M2B	Conventional	2-METHYL-2-BUTE	C5H10-6
2M1B	Conventional	2-METHYL-1-BUTE	C5H10-5
TAEE	Conventional	ETHYL-TERT-PEN	C7H16O-E2
2M1P	Conventional	2-METHYL-1-PENT	C6H12-D2
2M2P	Conventional	2-METHYL-2-PENT	C6H12-8
2M2EXP	Conventional		C8C100
C3M2P	Conventional	3-METHYL-CIS-2-P	C6H12-[illegible]

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.



User Defined Component Wizard

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: ETHANOL

Type: Conventional

Formula: C2H6O-2

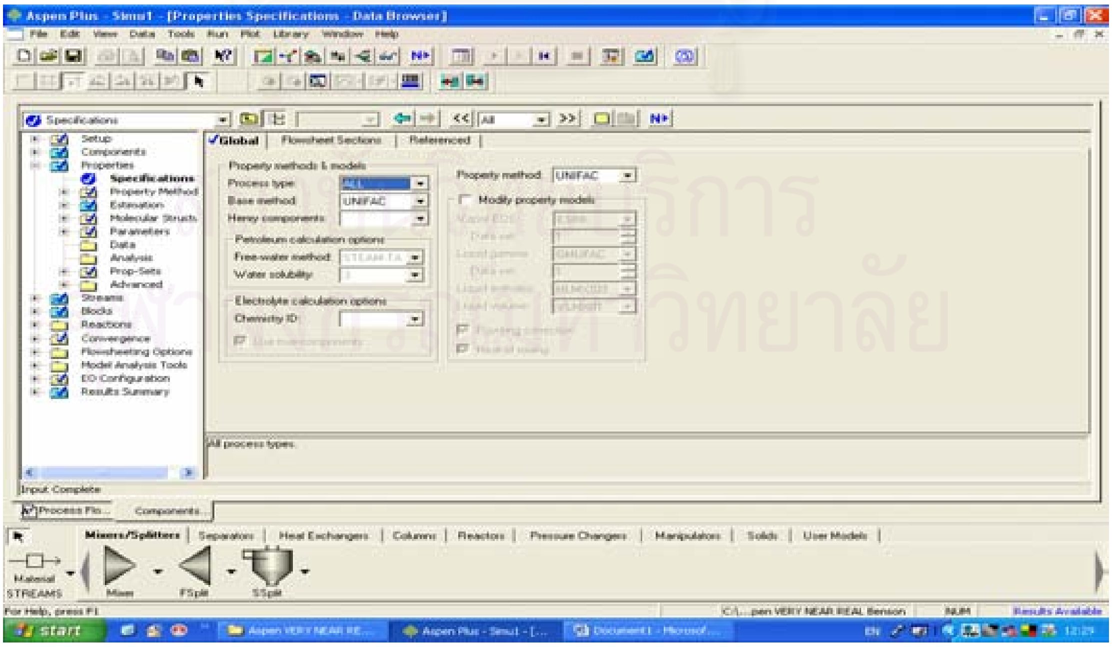
The required properties for Conventional components are

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.

Figure E-5 Define new components.

2.3 Type the formula and name of new components.



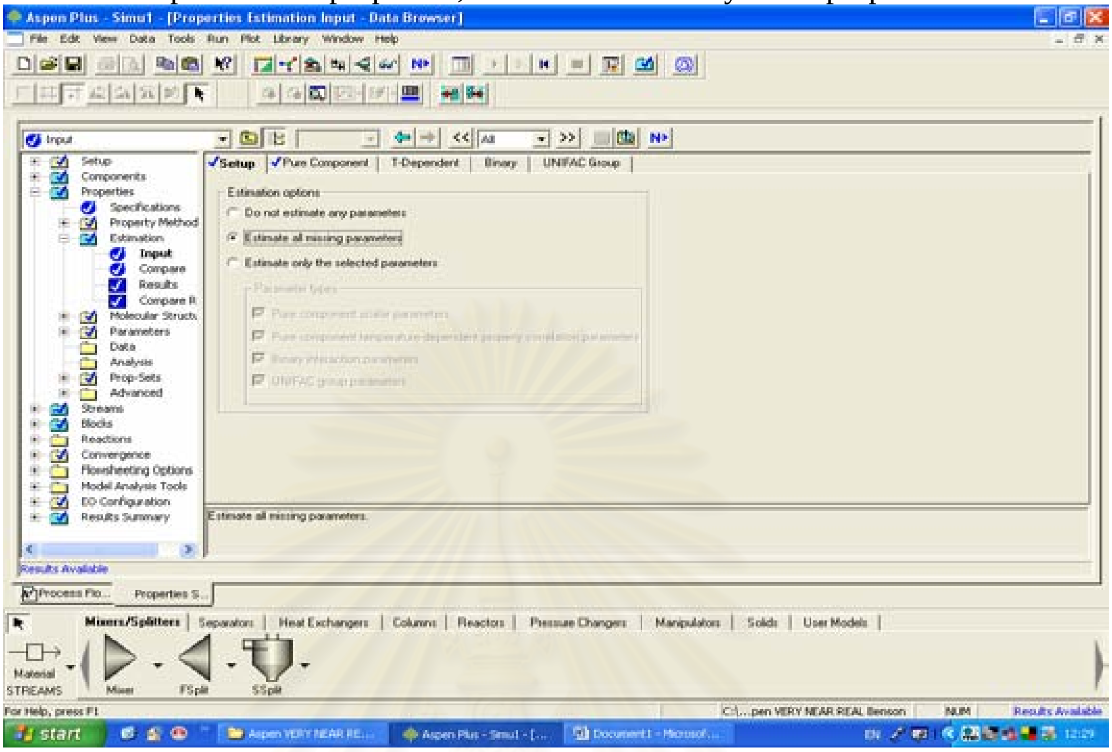
Process type: ALL

Base method: UNIFAC

Property method: UNIFAC

Figure E-6 Specification of thermodynamic method.

2.4 In specification properties, choose the thermodynamic properties.



Aspen Plus - Simu1 - [Properties Estimation Input - Data Browser]

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

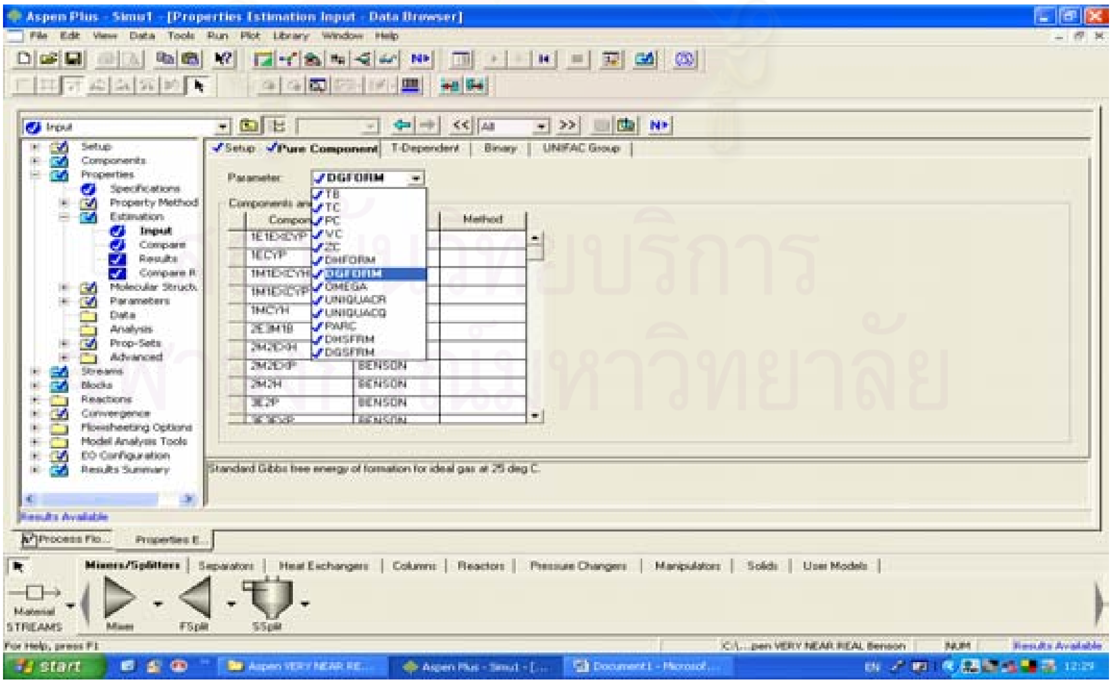
☑ Binary interaction parameters

☑ UNIFAC group parameters

Estimate all missing parameters.

Figure E-7 Click Estimate of missing parameters.

2.5 Estimation tab, tick Estimate all missing parameters.



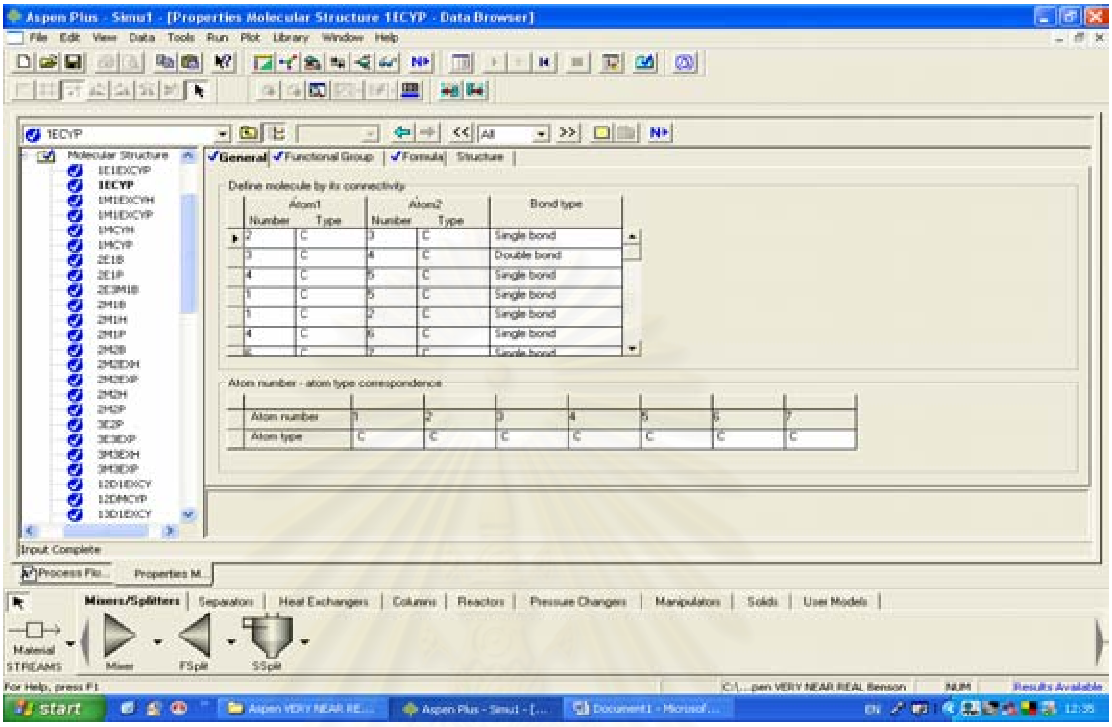
Aspen Plus - Simu1 - [Properties Estimation Input - Data Browser]

Parameter: DGFORM

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.



Define molecule by its connectivity

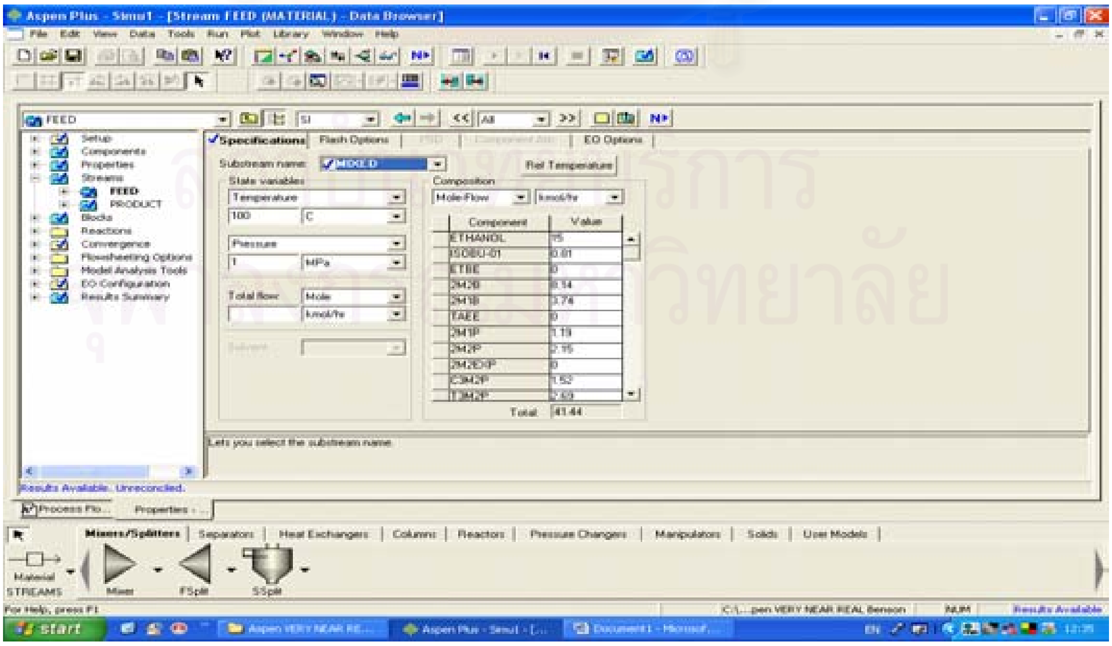
Atom1		Atom2		Bond type
Number	Type	Number	Type	
2	C	3	C	Single bond
3	C	4	C	Double bond
4	C	5	C	Single bond
1	C	5	C	Single bond
1	C	2	C	Single bond
4	C	6	C	Single bond
6	C	7	C	Single bond

Atom number - atom type correspondence

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

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).



Substream name: MIXED

State variables

Temperature: 100 C

Pressure: 1 MPa

Total flow: Mole kmol/hr

Composition: Mole-Flow kmol/hr

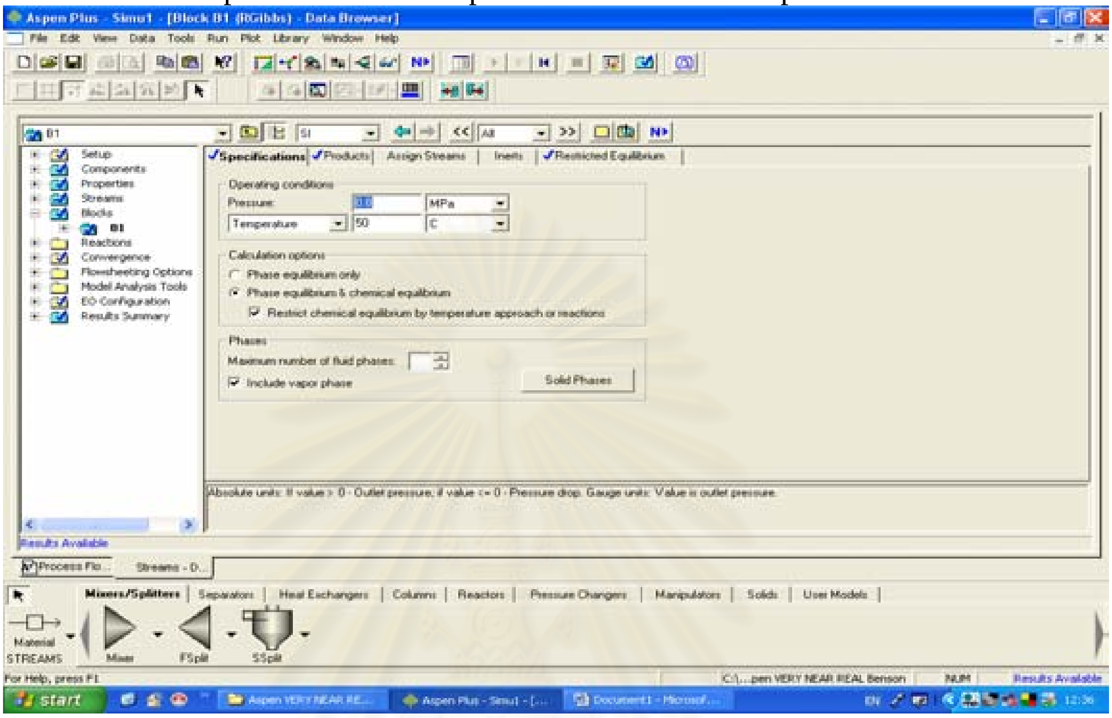
Component	Value
ETHANOL	15
ISOBU-01	0.01
ETBE	0
2M2B	8.34
2M1B	3.74
TAEE	0
2M1P	1.19
2M2P	2.15
2M2EXP	0
C3M2P	1.52
T3M2P	2.69

Total 41.44

Lets you select the substream name.

Figure E-10 Specification of feed stream.

2.8 This step showed that the specification of feed components.



Operating conditions
Pressure: [illegible] MPa
Temperature: 50 C

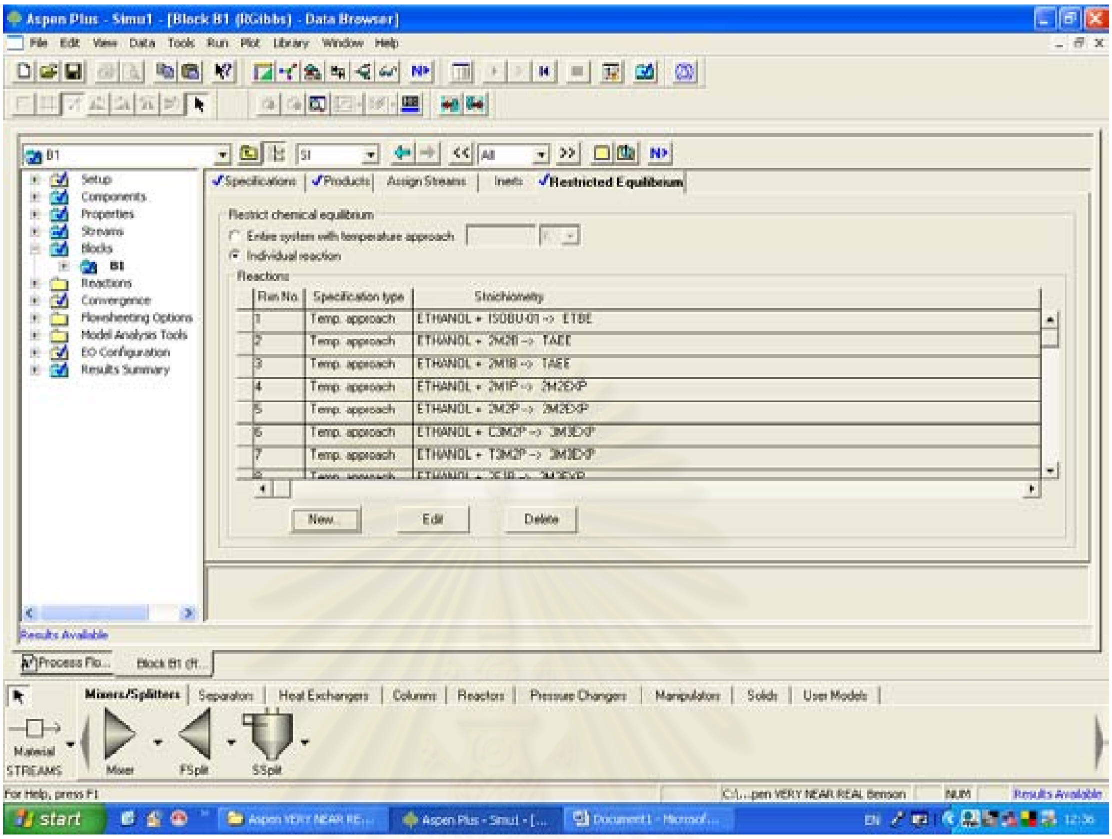
Calculation options
○ Phase equilibrium only
● Phase equilibrium & chemical equilibrium
☑ Restrict chemical equilibrium by temperature approach or reactions

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

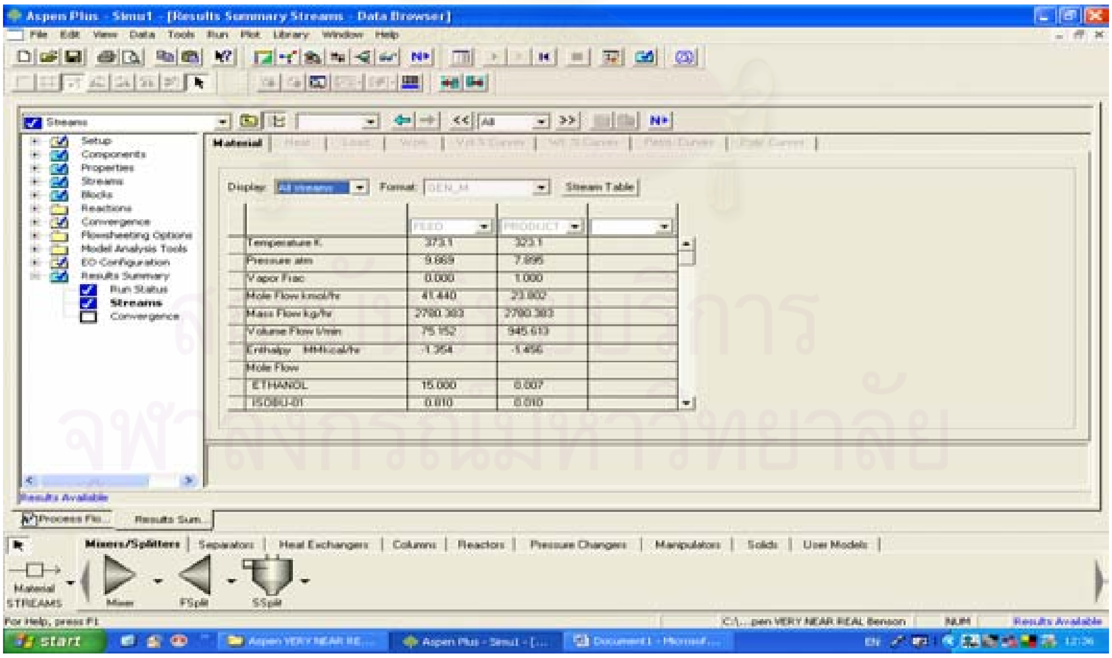
● Individual reaction

Reactions

Rxn No.	Specification type	Stoichiometry
1	Temp. approach	ETHANOL + ISOBU-01 --> ETBE
2	Temp. approach	ETHANOL + 2M2B --> TAEE
3	Temp. approach	ETHANOL + 2M1B --> TAEE
4	Temp. approach	ETHANOL + 2M1P --> 2M2EXP
5	Temp. approach	ETHANOL + 2M2P --> 2M2EXP
6	Temp. approach	ETHANOL + C3M2P --> 3M3EXP
7	Temp. approach	ETHANOL + T3M2P --> 3M3EXP

Figure E-12 Define reactions.

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



Display: All streams Format: GEN_M

	FEED	PRODUCT	
Temperature K	373.1	323.1	
Pressure atm	9.869	7.895	
Vapor Frac	0.000	1.000	
Mole Flow kmol/hr	41.440	23.802	
Mass Flow kg/hr	2780.383	2780.383	
Volume Flow l/min	75.152	945.613	
Enthalpy MMkcal/hr	-1.354	-1.456	
Mole Flow			
ETHANOL	15.000	0.007	
ISOBU-01	0.010	0.010	

Figure E-13 Checked results.

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

APPENDIX F

PROPERTIES OF COMPONENT

This chapter will showed the final result of each component. The result will be taken from the group contribution method and compare with the value from literature.

Table F-1 The normal boiling point of components.

Component	Joback's method (K)	Gani's method (K)	Literature (K)
ETHANOL	337.34	330.01	351
ISOBUTENE	287.48	263.13	266.85
ETBE	355.87	345.44	-
2M2B	317.84	314.70	304.25
2M1B	310.36	299.94	311.75
TAEE	378.75	379.12	-
2M1P	333.24	339.33	335.15
2M2P	340.72	343.85	326.75
2M2EXP	401.63	406.76	-
C3M2P	340.72	343.85	340.85
T3M2P	340.72	343.85	343.55
2E1B	333.24	331.14	337.85
3M3EXP	401.63	406.67	-
23DM1B	332.8	322.44	326.75
23DM2B	340.6	356.14	346.35
23DM2EXB	401.19	402.46	-
1MCYP	339.32	353.68	348.65
1M1EXCYP	400.23	413.75	-
2M1H	356.12	372.34	365.15
2M2H	363.6	376.19	368.35

2M2EXH	424.51	430.94	-
C3M2H	363.6	376.19	370.45
T3M2H	363.6	376.19	368.35
C3M3H	363.6	369.36	368.55
T3M3H	363.6	369.36	366.65
2E1P	356.12	365.37	367.15
3M3EXH	424.51	430.11	-
23DM1P	355.68	362.12	357.35
23DM2P	363.48	380.24	370.55
23DM2EXP	424.07	430.11	-
C34DM2P	363.16	362.19	362.35
T34DM2P	363.16	362.19	364.65
2E3M1B	355.68	350.58	359.45
23DM3EXP	424.07	418.99	-
24DM1P	355.68	356.26	354.75
24DM2P	363.16	362.19	356.45
24DM2EXP	424.07	418.99	-
3E2P	363.6	369.36	369.15
3E3EXP	424.51	430.94	-
233TM1B	352.89	347.82	350.75
233T2EXB	421.28	430.38	-
1ECYP	362.2	384.62	379.45
1E1EXCYP	423.11	437.24	-
12DMCYP	362.08	386.45	379.95
15DMCYP	361.76	373.35	375.15
12D1EXCY	422.67	428.59	-
13DMCYP	361.76	373.35	365.15
14DMCYP	361.76	373.35	366.35
13D1EXCY	422.67	428.59	-
1MCYH	362.2	384.73	383.15
1M1EXCYH	423.11	473.33	-

Table F-2 The critical temperature of components.

Component	Joback's method (K)	Gani's Method (K)	Ambrose's method (K)	Literature (K)
ETHANOL	499.11	489.28	577.05	513
ISOBUTENE	455.74	415.2	492.26	417.9
ETBE	531.48	514.79	609.36	-
2M2B	493.47	478.56	544.24	470
2M1B	479.88	462.48	531.43	470
TAEE	553.94	552.81	648.54	-
2M1P	503.41	506.02	570.61	506.5
2M2P	516.68	513.12	583.42	-
2M2EXP	576.09	580.48	687.72	-
C3M2P	516.68	513.12	583.42	-
T3M2P	516.68	513.12	583.42	-
2E1B	503.41	499.94	570.61	-
3M3EXP	576.09	580.48	687.72	-
23DM1B	507.18	486.52	569.86	501
23DM2B	520.28	525.09	583.21	524
23DM2EXB	579.70	581.82	686.96	-
1MCYP	508.75	546.5	439.73	542
1M1EXCYP	568.74	600.95	499.16	-
2M1H	526.43	541.1	609.79	-
2M2H	539.40	546.97	622.60	-
2M2EXH	598.00	604.48	726.90	-
C3M2H	539.40	546.97	622.60	-
T3M2H	539.40	546.97	622.60	-
C3M3H	539.40	542.13	622.60	-
T3M3H	539.40	542.13	622.60	-
2E1P	526.43	536.1	609.79	-
3M3EXH	598.00	604.48	726.90	-

23DM1P	530.10	530.43	609.04	-
23DM2P	542.90	552.38	622.39	-
23DM2EXP	601.47	609.03	726.14	-
C34DM2P	543.24	531.58	621.84	-
T34DM2P	543.24	531.58	621.84	-
2E3M1B	530.10	519.72	609.04	-
23DM3EXP	601.47	592.46	726.14	-
24DM1P	530.10	523.8	609.04	-
24DM2P	543.24	531.58	621.84	-
24DM2EXP	601.47	592.46	726.14	-
3E2P	539.40	542.13	622.60	-
3E3EXP	598.00	604.48	726.90	-
233TM1B	534.94	515.51	604.26	-
233T2EXB	606.03	623.25	721.36	-
1ECYP	531.68	575.07	469.38	-
1E1EXCYP	590.88	622.53	527.70	-
12DMCYP	535.00	579.59	469.22	-
15DMCYP	535.30	565.17	498.77	-
12D1EXCY	594.15	614.96	547.74	-
13DMCYP	535.30	565.17	498.77	-
14DMCYP	535.30	565.17	498.77	-
13D1EXCY	594.15	614.96	547.74	-
1MCYH	531.68	586.28	451.73	-
1M1EXCYH	590.88	631.21	518.67	-

Table F-3 The critical pressure of components.

Component	Joback's method (Atm)	Gani's Method (Atm)	Ambrose's method (Atm)	Literature (Atm)
ETHANOL	49.08	54.84	49.04	-
ISOBUTENE	43.68	38.96	43.02	39.47
ETBE	30.39	29.89	30.37	-
2M2B	38.59	34.72	38.04	33.75
2M1B	38.59	33.12	38.04	37.50
TAEE	27.39	27.27	27.37	-
2M1P	34.35	29.63	33.88	32.37
2M2P	34.35	29.8	33.88	-
2M2EXP	24.82	24.68	24.80	-
C3M2P	34.35	29.8	33.88	-
T3M2P	34.35	29.8	33.88	-
2E1B	34.35	28.54	33.88	-
3M3EXP	24.82	24.68	24.80	-
23DM1B	34.35	28.82	33.88	31.97
23DM2B	34.80	31.42	33.88	33.16
23DM2EXB	24.82	25.76	24.80	-
1MCYP	37.10	37.69	3112.71	37.40
1M1EXCYP	26.49	29.45	26.47	-
2M1H	30.76	26.69	30.37	-
2M2H	30.76	26.83	30.37	-
2M2EXH	22.59	22.46	22.57	-
C3M2H	30.76	26.83	30.37	-
T3M2H	30.76	26.83	30.37	-
C3M3H	30.76	25.86	30.37	-
T3M3H	30.76	25.89	30.37	-
2E1P	30.76	25.76	30.37	-

3M3EXH	22.59	22.46	22.57	-
23DM1P	30.76	26.12	30.37	-
23DM2P	31.14	27.19	30.37	-
23DM2EXP	22.59	23.49	22.57	-
C34DM2P	30.76	26.14	30.37	-
T34DM2P	30.76	26.14	30.37	-
2E3M1B	30.76	25.11	30.37	-
23DM3EXP	22.59	22.34	22.57	-
24DM1P	30.76	26.53	30.37	-
24DM2P	30.76	26.14	30.37	-
24DM2EXP	22.59	22.34	22.57	-
3E2P	30.76	25.89	30.37	-
3E3EXP	22.59	22.46	22.57	-
233TM1B	30.76	26.36	30.37	28.52
233T2EXB	22.59	25.5	22.57	-
1ECYP	33.09	33.44	14667.35	-
1E1EXCYP	24.04	26.53	24.02	-
12DMCYP	33.51	33.89	32.64	-
15DMCYP	33.09	33.41	27.26	-
12D1EXCY	24.04	26.51	2324.04	-
13DMCYP	33.09	33.41	27.26	-
14DMCYP	33.090	33.41	27.26	-
13D1EXCY	24.04	26.51	2324.04	-
1MCYH	33.09	32.78	14667.35	35.22
1M1EXCYH	24.04	26.07	24.02	-

Table F-4 The standard Gibbs of formation of components.

Component	Joback's method (kJ/mol)	Gani's Method (kJ/mol)	Benson's method (kJ/mol)	Literature (kJ/mol)
ETHANOL	-170.86	-173.21	-156.95	-167.73
ISOBUTENE	106.05	59.41	54.50	58.2
ETBE	29.36	-110.91	-142.97	-121.15
2M2B	150.81	57.69	51.66	58.4
2M1B	114.47	67.40	120.31	65
TAEE	29.36	-102.29	-134.19	-120.9
2M1P	114.47	75.60	69.33	-
2M2P	159.23	65.64	60.05	64.7
2M2EXP	29.36	-94.05	-126.03	-
C3M2P	159.23	65.64	60.05	73.27
T3M2P	159.23	65.64	55.85	71.34
2E1B	114.47	75.35	71.29	-
3M3EXP	29.36	-94.05	-122.68	-
23DM1B	164.41	71.58	62.12	79.09
23DM2B	102.28	73.47	52.82	75.91
23DM2EXB	87.72	-90.96	-130.92	-
1MCYP	159.23	101.29	105.33	-
1M1EXCYP	29.36	-55.81	-82.44	-
2M1H	114.47	83.84	77.48	-
2M2H	159.23	73.88	68.21	-
2M2EXH	29.36	-85.85	-117.88	-
C3M2H	159.23	73.88	68.21	-
T3M2H	159.23	73.88	64.01	-
C3M3H	159.23	73.63	68.45	-
T3M3H	159.23	73.63	64.25	-
2E1P	114.47	83.59	77.73	-

3M3EXH	29.36	-85.85	-116.25	-
23DM1P	172.83	79.53	68.56	-
23DM2P	110.7	81.46	57.78	-
23DM2EXP	87.72	-83.01	-121.14	-
C34DM2P	209.17	69.87	61.00	-
T34DM2P	209.17	69.87	56.80	-
2E3M1B	172.83	79.57	70.52	-
23DM3EXP	87.72	-90.20	-121.14	-
24DM1P	172.83	79.49	69.24	-
24DM2P	209.17	69.87	61.00	-
24DM2EXP	87.72	-90.20	-122.77	-
3E2P	159.23	73.63	68.45	-
3E3EXP	29.36	-85.85	-108.46	-
233TM1B	222.07	81.00	67.22	-
233T2EXB	29.36	-72.80	-122.31	-
1ECYP	159.23	109.53	113.73	-
1E1EXCYP	29.36	-47.57	-70.94	-
12DMCYP	110.7	116.14	100.58	101.8
15DMCYP	217.59	104.89	104.56	-
12D1EXCY	87.72	-52.21	-80.89	-
13DMCYP	217.59	104.89	104.56	-
14DMCYP	217.59	104.89	103.53	-
13D1EXCY	87.72	-52.21	-84.24	-
1MCYH	159.23	95.64	102.13	-
1M1EXCYH	29.36	-61.50	-90.05	-

VITAE

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