

KLM Technology Group Practical Engineering Guidelines for Processing Plant Solutions	 SOLUTIONS, STANDARDS AND SOFTWARE www.klmtechgroup.com	Page : 1 of 75
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KLM Technology Group #03-12 Block Aronia, Jalan Sri Perkasa 2 Taman Tampoi Utama 81200 Johor Bahru	Kolmetz Handbook of Process Equipment Design BTX EXTRACTION UNIT DESIGN, SIZING AND TROUBLESHOOTING (ENGINEERING DESIGN GUIDELINE)	Co Author: Rev 01 – Yulis Sutianingsih Editor / Author Karl Kolmetz

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INTRODUCTION

Benzene, Toluene, and Xylene are become the lowest molecular weight of the aromatic class. They are very beneficial for petrochemical feedstocks. They are considered as one group because in real application, benzene, toluene and xylene are produce in the same process. The familiar name is “BTX”.

Originally produced from commercial pyrolysis of coal, BTX production shifted to gasoline production. These aromatic compounds have such high value octane number that made them good components to be mixed with gasoline products to alter its octane number as market requirements

Benzene, Toluene and Xylene combined produce one of the largest aromatic volumes that is used in the petrochemical industry. Toluene could be converted to Benzene to fulfilled market demand by hydroalkylation process. Products separation is required to split each into pure components. Thus, separation process could be consisted of: Extraction, Distillation, Crystallization or combination of all of those processes.

Properties

Benzene

Benzene is an aromatic compound with single ring and composed of six carbon atoms and six hydrogen atoms (C₆H₆, Figure 1). Benzene is colorless and classes as flammable liquid with boiling point at 80.1°C and flash point 5.5°C. Styrene, phenol, and cyclohexane are chemicals derived from benzene which could be used for manufacturing several daily products including : dyes, detergents, plastics, resins, and insecticides. Benzene is very toxic but also a good solvent agent and has high octane rating for gasoline blending. Table 1 to Table 4 are providing details data of physical – chemical information of Benzene.

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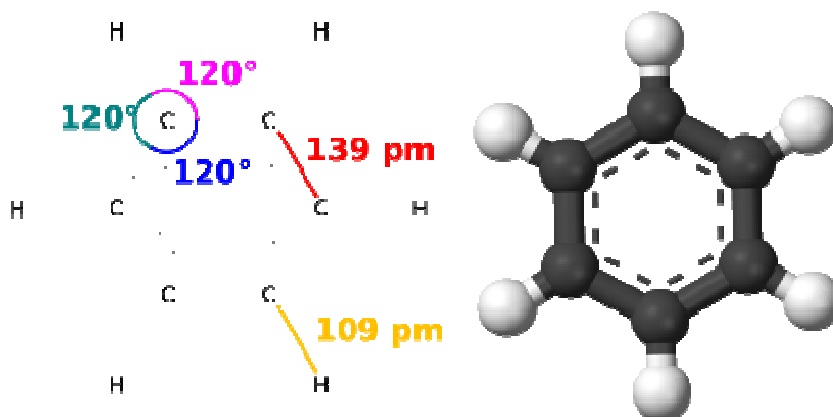


Figure 1. Benzene molecule

Table 1. Physical data of C₆ – C₈ aromatics

Compounds	Molecular weight (Mr)	Density (kg/m ³)	Melting point (°C)	Boiling point (°C)	Flash point (°C)
Benzene	78.11	879.01	5.533	80.099	-11
Toluene	92.13	866.94	-94.991	110.626	4.0
Ethylbenzene	106.16	866.90	-94.975	136.186	15
o-xylene	106.16	880.20	-25.182	144.411	17
m-xylene	106.16	864.17	-47.872	139.104	23.2
p-xylene	106.16	861.05	13.263	138.351	25

Table 2. Binary azeotrope mixtures of benzene

Component B	Benzene composition (% wt)	Azeotrope temperature (°C)
Water	91.17	69.25
Methanol	60.4	58.34
Acetonitrile	60.0	73.7
Acetic acid	98.0	80.5
Ethyl alcohol	67.6	68.24
Isopropyl alcohol	66.7	71.92
Propyl alcohol	83.1	77.12

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Cyclohexane	85.0	79.45
	55.0	77.5
n-Hexane	5.0	68.87

Benzene is a basic aromatic class and is one of the largest organic chemicals that had been produced in the United States. Benzene is thermally stable and formed at temperatures of 500°C. Elevating temperature can make benzene decompose thermally.

Condensation reactions could take place in association with several minerals like lead, iron and other catalytic materials such as vanadium to form diphenyl and any other polyaromatic components. Oxidation of benzene is severe under the presence of water and carbon dioxide. Phenol can be obtained in low yield by high-temperature oxidation of benzene with air. Substitution reaction is one of the most important reactions on benzene that could produce disubstituted benzene with three possible isomers.

Table 3. Ternary azeotrope mixtures of benzene

Component		Benzene (% wt)	B (% wt)	Azeotrope (°C)
B	C			
Water	Ethyl alcohol	74.1	7.4	64.86
Water	Allyl alcohol	82.1	8.6	68.3
Water	n-isopropyl alcohol	82.4	8.6	68.48
Water	Isopropyl alcohol	73.8	7.5	66.51
Water	2-butanone	73.6	8.9	68.9
Water	Sec-butyl alcohol	85.55	8.63	69.0
Water	Tert-butyl alcohol	70.5	8.1	67.3
Chloroform	1,2-dichloroethane	66.4	5.0	79.2
Water	Acetonitrile	68.5	8.2	66.0

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Table 4. Octane rating of benzene and related components

Component B	Boiling point (°C)	Octane Rating
Benzene	80.1	98
Cyclohexane	81.4	83
Toluene	110.6	120
Ethylbenzene	136.1	107
o-xylene	144.4	120
m-xylene	139.1	115
p-xylene	138.4	116
Cumene	152.4	113

As in general, production of benzene and its homologues such as toluene and xylene (BTX) are below 15% on naphtha fractions from petroleum refinery plant with benzene contents in the fractions maximum of 50% of the total aromatic content. Table 5 shows the aromatic, naphthenic, and paraffinic contents of several type petroleum and naphtha fractions.

Table 5. Petroleum properties

Properties	Petroleum A	Petroleum B	Petroleum C
Crude gravity (°API)	34 – 34.9	37.4	34.1
C₆ and lighter (% vol)	1.6	3.3	1.5
Light debutanized naphtha yield (% vol)	13.7	13.23	9.3
Boiling point (°C)	Up to 126	31 – 105	Up to 93
Aromatics content (% vol)	5	3.1	2.4
Naphthenes content (% vol)	5	30.5	12.3
Paraffins content (% vol)	90	66.4	85.3
Sulphur content (% wt)	1.63	0.31	1.72

Hence, addition, alkylation and hydrogenation are several other reactions that could be reacted to a benzene molecule. The reactions generally take place at elevated temperature and pressure under the presence of catalyst. Ethylbenzene could be obtained from alkylation of benzene with ethylene in the presence of a catalyst. Hydrogenation of benzene at elevated temperature and pressure may produce cyclohexane. Whereas

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dehydrogenation of ethylbenzene to form styrene is necessary in the kinetic and thermodynamic perspective due to the endothermic operating conditions.

Toluene

Toluene is known due to its derivative compounds trinitrotoluene (TNT) in which extensively used during World War I and World War II. Production of sufficient quantities of toluene was obtained by catalytic reforming process where naphtha fractions from crude petroleum is converted to reformat along with high aromatic content. Extraction and extractive distillation had been developed to isolate pure toluene from reformat. Toluene (Figure 3) could be added to gasoline fuel as a mixture with other aromatics due to high resistance to knocking event. Table 6 to Table 8 listed physical and chemical data of toluene.

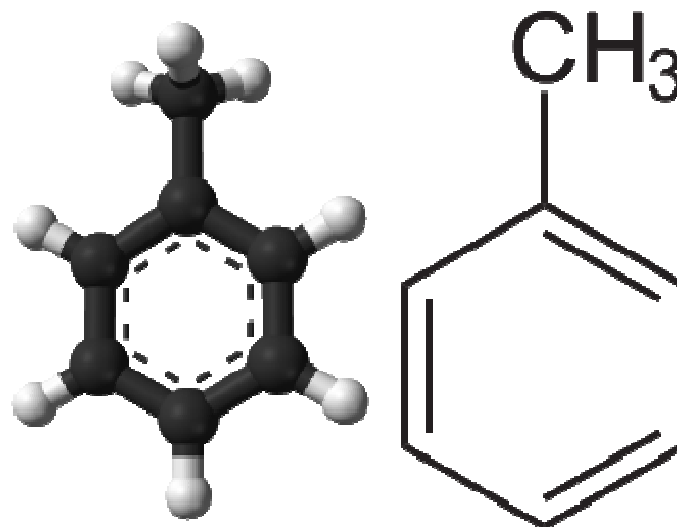


Figure 3. Toluene Molecule

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Table 6. Properties of Toluene

Properties	Value
Molecular weight (Mr)	92.13
Melting point (°C)	-94.991
Boiling point (at 100 kPa)	110.625
Critical temperature (°C)	320.8
Critical pressure (MPa)	4.133
Critical compressibility	0.260
Critical molecular volume (/mol)	0.321
Density at 100 kPa, 25°C (kg/m ³)	863.1
Viscosity at 100 kPa, 20°C (mPa.s)	0.5864
Flash point (°C)	4

Table 7. Binary azeotrope of Toluene

Component	Toluene composition of azeotrope (% wt)	Boiling point (°C)	
		Component (% wt)	Azeotrope
Water	79.7	100	84.1
Methanol	31	64.7	63.8
Acetic acid	66	118.5	105.0
Ethanol	33	78.3	76.6
Glycol	93.5	197.4	110.2
Ethylenediamine	70	116.9	103
Propanol	49	97.3	92.5
Butanol	73	117.8	105.7
Isobutanol	55.5	108.0	100.9
Tert-Amyl alcohol	44	101.7	100.0
Isoamyl alcohol	88	131.3	110.0

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Toluene had another name called “methylbenzene” composed by seven carbon atoms and eight hydrogen atoms (C₇H₈). Toluene is a colorless and flammable with low viscosity and smells like benzene. Toluene is a good solvent for oils, tars, sulphur, fats and so on. Toluene is completely miscible with most organic solvents like alcohols, phenols, ethers and ketones. Toluene slightly soluble in water.

Table 8. Ternary azeotrope of Toluene

Components	Boiling point (°C)		Composition in azeotrope (% wt)		
	Component	Azeotrope	Toluene	A	B
A Water	100	76.3	48.7	13.1	38.2
B Isopropanol	82.3				
A Butanol	117.8	108.7	67.4	11.9	20.7
B Pyridine	115.5				
A Pyridine	115.5	110.2	87.3	8.6	4.1
B Isoamyl alcohol	131.3				

At most cases, toluene has a similar chemical properties with benzene. Furthermore, methyl group provides additional reactivity. Alkylation of toluene with propylene gives methylcumene (cymenes). Meanwhile, cumene hydroperoxides could be obtained by toluene saponification for acetone production.

Xylene

Another homologues of benzene is xylene. Xylene composed by eight carbon atoms and ten hydrogen (C₈H₁₀) atoms with boiling points in range of 135 – 145°C depend upon mixture of isomers which mainly consisted of at least three isomeric components : dimethylbenzenes and ethylbenzenes (Figure 4).

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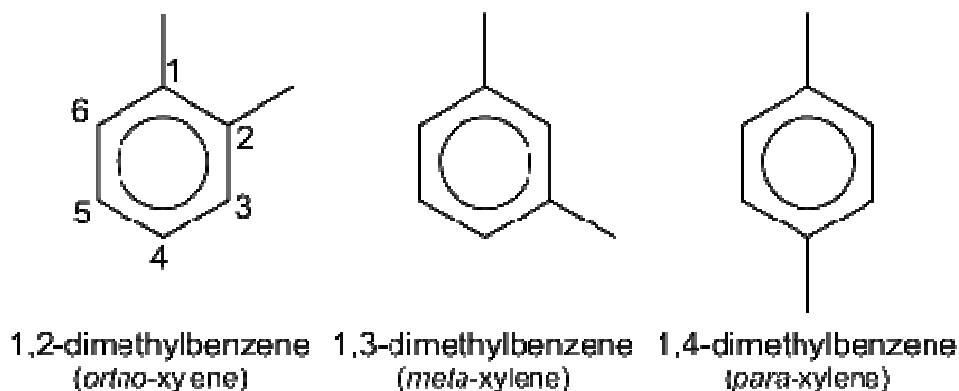


Figure 4. Xylene

Xylene always produce as a mixture along with other isomer. Disproportionation of toluene is another path to produce xylene compounds. Xylenes are good for motor fuels due to their high knock resistance.

Isomeric xylenes and ethylbenzene form azeotropic mixtures with water and numerous organic compounds (Table 10 and Table 11). Absorption properties of exylene are of technical interest due to the significant differences in the solubilities of various gases as a function of temperature. Table presents details of xylene and its isomer physical data.

Table 10. Binary azeotrope of Xylene

Component A	Aromatic	Azeotrope	
		Boiling point (°C)	Composition of A (% wt)
Water	m-xylene	94.5	40
	ethylbenzene	33.5	33
Methanol	p-xylene	64.0	5
Butanol	Ethylbenzene	115.85	65
Isobutanol	Ethylbenzene	125.7	49
Ethylene glycol	o-xylene	135.7	7

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Glycol	o-, m-, p-xylene and ethylbenzene	133 – 139	14
Acetic acid	o-, m-, p-xylene and ethylbenzene	114 – 116	66 – 76
Phenol	m-xylene	133	18

Table 11. Properties of Xylene and its isomer

Properties	o-xylene	m-xylene	p-xylene	Ethylbenzene
Molecular weight (Mr)	106.16	106.16	106.16	106.16
Boiling point, at 1 bar (°C)	144.4	139.1	138.4	136.2
Critical temperature (°C)	357.1	343.6	342.8	344.0
Critical pressure (bar)	35.20	35.47	34.45	37.27
Critical compressibility	0.260	0.270	0.250	0.260
Critical molar volume (/mol)	0.380	0.390	0.370	0.371
Melting point (°C)	- 25.182	- 47.87	13.26	- 95.00
Density at 1 bar (kg/m³)				
At 20°C	880.2	864.2	861.0	867.0
At 25°C	876.0	859.9	856.7	862.4
Dynamic viscosity at 20°C (mPa.s)	0.809	0.617	0.644	0.6783

Oxidation of toluene and isomers obtain dicarboxylic acids. Phthalic acids is produced industrially from o-xylene, isophthalic acid from m-xylene whereas terephthalic acid from p-xylene. The reaction goes under gas and liquid phases and have been widely applied on many petrochemical plant around the world. Nitration of o- and m-xylenes provides a route to xylidines following hydrogenation of the initially formed dimethylnitrobenzene isomers.

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Xylidines typically used as intermediates in dye and rubber additive production. Sulfonation of m-xylene and subsequent decomposition of the sulfonic acid derivatives gives 3,5- and 2,4-xylenols providing starting materials for insecticides and herbicides.

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DEFINITION

Benzene – An aromatic compound with single ring and composed of six carbon atoms and six hydrogen atoms (C₆H₆).

Extraction - A process for separating components dissolved in a liquid feed by contact with a second liquid phase.

Loading Capacity – A term refers to a maximum content of solute within the extract before it separate. Loading capacity could be determined by the point in which all the extractant in solution is completely occupied by solute.

NMP – N-methyl 1-2-pyrrolidinone, refer to the one a kind of extractive distillation process in which main solvent is N-methyl 1-2-pyrrolidinone.

Partition Ratio – A proportion that show a minimum amount of solvent that allowed for extraction process.

Saturated-chain hydrocarbon – A kind of hydrocarbon that aim to paraffinic and cycloparaffinic compounds.

TEG – Tetraethylene Glycol, refer to the one a kind of extractive distillation process in which main solvent is tetraethylene glycol.

Toluene – Another name of “methylbenzene” composed by seven carbon atoms and eight hydrogen atoms (C₇H₈)

Unsaturated-chain hydrocarbon – A kind of hydrocarbon which could be produced by fluid catalytic cracking units, steam cracking and low polymerization of low molecular weight components.

Xylene – An aromatic compound with single ring and composed by eight carbon atoms and ten hydrogen atoms (C₈H₁₀).

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NOMENCLATURE

C_1	: concentration of solute in first liquid phase (% wt)
C_2	: concentration of solute in second liquid phase (% wt)
K	: Partition ratio
K_i	: Partition ratio of solute i
K_j	: Partition ratio of solute j
L_0	: Feed stream input (kg/h)
L_1	: Raffinate stream (kg/h)
L_N	: Raffinate stream (kg/h)
S	: pure solvent (lb)
V_1	: Extract stream (kg/h)
V_1	: Solvent stream input (kg/h)
V_2	: Extract stream (kg/h)
V_{N+1}	: Solvent stream input (kg/h)
W	: stock to be treated (lb)
x_A	: fraction mass A.
x_{A0}	: Fraction A on feed
x_{A1}	: Fraction A on raffinate
x_{AM}	: Fraction A in mixture point
x_{AN}	: Fraction A on raffinate
x_B	: fraction mass B.
x_C	: fraction mass C.
x_{C0}	: Fraction C on feed
x_{C0}	: Fraction C on feed
x_{C1}	: Fraction C on raffinate
x_{CM}	: Fraction C on mixture point
x_{CN}	: Fraction C on raffinate
y_{A1}	: Fraction A on extract
y_{A2}	: Fraction A on solvent
y_{C1}	: Fraction C on extract
y_{C2}	: Fraction C on solvent
y_{CN+1}	: Fraction C on solvent

SYMBOLS

α : Selectivity solute i over solute j

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