Selection of Appropriate Thermodynamic Equations for Simulation of Separation Columns of Vinyl Chloride Unit of Iran Bandar Imam Petrochemical Company (BIPC)

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Abstract

In this paper, Peng-Robinson, Soave-Redlich-Kwong, Wilson, NRTL and UNIQUAC thermodynamic equations are considered for simulation of ten different separation columns of vinyl chloride unit of Iran Bandar Imam petrochemical company. The separation columns are related to different vinyl chloride unit sections namely: Ethylene Dichloride Recovery (EDC Recovery) & Oxychlorination Ethylene Dichloride Washing (OXY EDC Washing), O-EDC Purification, EDC Cracking & Vinyl Chloride Purification (VC Purification), Waste Water Treatment & VC Refining and HCl Recovery sections. Simulated quantities are: temperature, flow rate and average molecular weight of outlet flows of the mentioned separation columns. The results show that Wilson equation is the most appropriate equation for simulation of the separation columns of vinyl chloride unit.

Key Words: Equation of State, Activity Coefficient Equation, Phase Equilibria, Vinyl Chloride Unit, Simulation

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Introduction

Selection of appropriate equation of states or activity coefficient equations for phase equilibrium calculations has a lot of effects on precision and accuracy of the calculated results. It is obvious that any equation of state or activity coefficient models have some application limitations and one can not use them for any systems at any temperature, pressure or compositions. Therefore, one has to select the appropriate thermodynamic models for modelling and simulations of a system before any calculations.

In this paper the ability of six different thermodynamic equations for simulation of separation columns of vinyl chloride (VC) unit of Iran Bandar Imam Petrochemical Company (BIPC) are considered. These equations are Peng- Robinson [1], Soave-Redlich- Kwong [2, 3], Wilson [4], NRTL [5] and UNIQUAC [6]. The reason of selection of these equations is that there is a lot of consistency between these equations and the hydrocarbon species those the VC unit is in related with them. In simulation procedure, the flow rates, temperature and molecular weights of outlet streams of any separation columns are selected as calculation targets.

Theoretical

For selection of an appropriate equation of state for simulation of separation columns of vinyl chloride unit of BIPC, three different quantities are calculated by five equation of states or activity coefficient equations. These quantities are composition error, temperature error and molecular weight error. Finally, summation of these quantities is calculated. Thermodynamic equation with the minimum error is selected as the appropriate equation for simulation of the considered separation column.

1. Composition error

Composition error for every stream is determined by the following relation:

$$Err_F = \sum_{i=1}^{NP} \left| \frac{m_i' - m_i}{m_i} \right| \times 100 \times \frac{m_i}{m_T} \quad (1)$$

where, m_i' and m_i are calculated mole flow rate of component *i* and its experimental value, respectively. m_T is total flow rate of the stream and *NP* is the number of components in the stream.

2. Temperature error

The temperature error is the relative percent error of the simulated temperature of a specific stream. This error is defined as follows:

$$Err_T = \left| \frac{T' - T}{T} \right| \times 100 \quad (2)$$

where, T' and T are simulated and experimental temperature of the stream in Kelvin.

3. Molecular weight error

Same as temperature error, molecular weight error is the relative percent error of the simulated molecular weight of a specific stream and is defined as follows:

$$Err_{MW} = \left| \frac{MW - MW'}{MW} \right| \times 100 \quad (3)$$

In the above relation MV' and MV are simulated and experimental mean molecular weight of the considered stream, respectively.

4. Total error

For a specified stream, the total error is obtained by the following relation:

$$Err = Err_F + Err_T + Err_{MW} \quad (4)$$

We selected an equation of state as the best equation for simulation when the following equation was minimized:

$$Error_{(EOS)} = \frac{\sum_{I=1}^{NS} Err_{[I]} \times M_{[I]}}{\sum_{I=1}^{NS} M_{[I]}} \quad (5)$$

where, $M_{[I]}$ and $Err_{[I]}$ are mole flow rate and total error of the stream *I*, respectively. *NS* is total number of the exit streams from the separation column and $Error_{(EOS)}$ is equation of state or activity coefficient equation error which was used in simulation calculations.

Results and Discussion

In this work, separation columns of the following units are considered:
ethylene dichloride recovery (EDC recovery) and Oxychlorination Ethylene Dichloride Washing (OXY EDC washing), O-EDC purification, EDC cracking and Vinyl Chloride Purification (VC purification), waste water treatment and VC refining and finally HCl recovery units. For simulation of the columns of the mentioned units, the data of the feeds and products of each column is used. The target is minimizing the value of the quantities which were introduced above for any outlet streams with using the different thermodynamic equations.
Components of the outlet streams for different separation columns of the above mentioned units are reported in Table 1 and Table 2. Peng- Robinson [1], Soave-Redlich- Kwong [2, 3], Wilson [4], NRTL [5] and UNIQUAC equations are used for simulation. The best results are obtained by Wilson equation.

Table 1. Components of Outlet streams of EDC-Recovery and OEDC-Purification units

EDC Recovery		**OEDC purification**			
EDC Absorber	Stripper Column	Dehydration column	Light column	Heavy column	Recovery column
Ethylene	Ethyl Chloride	Ethyl Chloride	Vinyl chloride	1,1 dichloro ethane	Ethylene dichloride
Nitrogen	trans-DiChloro Ethylene	Trans-dichloro ethylene	1,1 dichloro ethane	Cis-dichloro ethylene	TriChloro Ethane
Oxygen	Cis – DiChloro Ethylene	Cis – DiChloro Ethylene	Cis-dichloro ethylene	chloroprene	Tetrachloro ethane
Ethyl Chloride	Ethylene DiChloride	Chloroform	chloroprene	chloroform	water
Trans-dichloro	Chloroform	Carbon tetrachloride	chloroform	Methallyl chloride	
Cis-dichloro ethylene	TriChloro Ethylene	benzen	Methallyl chloride	Carbon tetrachloride	
chloroform	TriChloro Ethane	Ethylene Dchloride	Carbon tetrachloride	benzen	
Ethylene Dchloride	Chloral	TriChloro Ethylene	benzen	Ethylene dichloride	
TriChloro Ethylene	Carbon TetraChloride	TriChloro Ethane	Ethylene dichloride	Trichloro ethylene	
Trichloro ethane	Water	water	Trichloro ethylene	TriChloro Ethane	
chloral		1,1 dichloro ethane	TriChloro Ethane	Tetrachloro ethane	
Carbon tetrachloride		chloroprene	Tetrachloro ethane	water	
Carbon MonOxide		Methallyl chloride	water		
Carbon DiOxyde		Tetrachloro ethane			
Water					

Table 2. Components of Outlet streams of EDC-Cracking, VC Refinary HCl Recovery Units

EDC & VC	**Cracking Purification**	**Waste Water Treatment & VC Refining**	**HCl Recovery**
HCl Column	VC Column	VC Refinary Column	HCl Refinary Column
Hydrogen	Hydrogen Chloride	Vinyl Chloride	Hydrogen Chloride
Ethylene	Methyl Chloride	Ethylene Dichloride	Water
Acetylene	Vinyl Chloride		
Hydrogen Chloride	1,1 dichloro ethane		
Methyl Chloride	Cis–DiChloro Ethylene		
Vinyl Chloride	chloroprene		
1,1 dichloro ethane	Chloroform		
Cis–DiChloro Ethylene	Methallyl chloride		
chloroprene	Carbon tetrachloride		
Chloroform	benzen		
Methallyl chloride	Ethylene Dchloride		
Carbon tetrachloride	TriChloro Ethylene		
benzen	TriChloro Ethane		
Ethylene Dchloride	Tetrachloro ethane		
TriChloro Ethylene			
TriChloro Ethane			
Tetrachloro ethane			

The total calculated errors for each separation columns are reported in table 3 and a comparison between the errors which are obtained by different equations is shown in figure 1.

Table 3. Calculated errors for different separation columns by using five thermodynamic equation

	Peng-Robinson	SRK	Wilson	NRTL	UNIQUAC
EDC Recovery & EDC Washing					
EDC Aborber	3.683	3.752	3.338	4.424	3.476
Stripper	13.018	13.363	11.400	12.663	12.787
O-EDC Purification					
Dehydration Column	7.316	7.607	6.170	9.718	6.523
Light Column	4.020	4.291	2.010	2.448	2.240
Heavy Columns	3.070	3.404	0.637	0.613	0.650
Recovery Column	6.532	7.422	4.320	4.507	4.381
EDC Cracking & VC Purification					
HCl Column	1.993	1.686	0.492	0.601	20.566
VC Column	0.359	0.457	0.407	0.416	0.411
Waste Water Treatment & VC Refining					
VC Refinary Column	1.869	1.783	1.357	1.358	1.361
HCl Recovery					
HCl Refinary Column	12.847	13.335	11.422	11.422	11.662

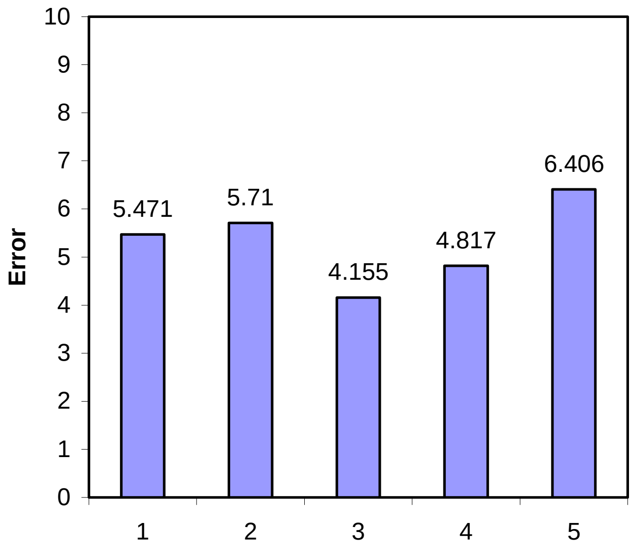

Figure 1. Error for different equations: 1. Peng-Robinson, 2. Soave-Redlich-Kwong, 3. Wilson, 4. NRTL, 5. UNIQUAC

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