Review Article

Separation of Light Hydrocarbons: A Minireview

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A R T I C L E   I N F O

**A B S T R A C T**

Separation of light hydrocarbons (LHs) is one of the most important and mostly energy intensive petrochemical processes. Several techniques have been developed industrially based on traditional separation methods such as distillation and extraction. However, they mainly suffer from high-energy consumption and low efficiency. Adsorptive separation using porous solid materials and membrane separation are the promising processes to separate the mixture of light hydrocarbons comprising paraffin/olefin mixtures of $C_1/C_2/C_3$ hydrocarbons. Introducing and developing new porous adsorbents for selective separation of LHs is highly needed because of competitive adsorption and challenging separations that are arising from the similarity in some structural and physicochemical properties of LHs. In addition, separation under the mild condition is of great importance for the application in industry. In this review, we discussed some methods for separation of LHs mixtures and highlighted the recent advances in the separation techniques based on using porous structures especially metal organic frameworks in the form of porous adsorbents and membranes.

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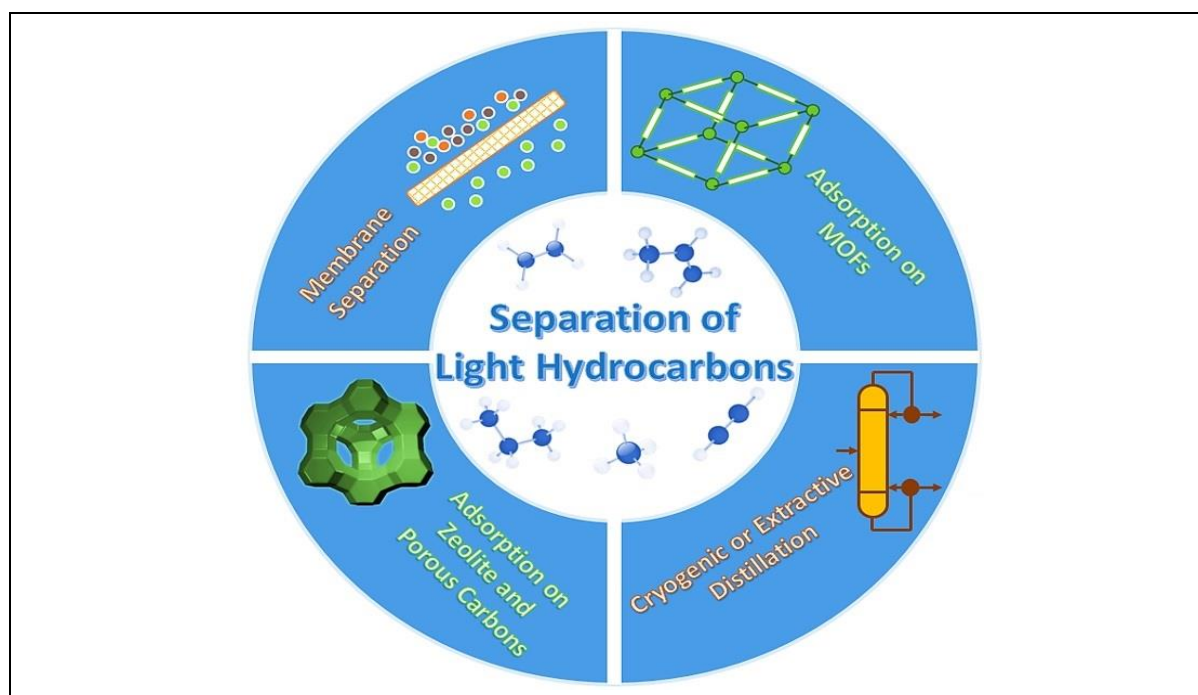
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Introduction

Light hydrocarbons mainly include methane (CH_4), acetylene (C_2H_2), ethylene (C_2H_4), ethane (C_2H_6), propene (C_3H_6) and propane (C_3H_8). Natural gas as a clean energy mainly contains 75-90% of CH_4 and the remaining is higher hydrocarbons, such as ethane, ethylene, and acetylene, and other impurities [1]. Refinery gas mainly comprises of CH_4 and C_2-C_4 light hydrocarbons with some contaminates including H_2, inert gases, H_2S or CO_2, H_2O and some quantities heavier hydrocarbons such as C_5. Table 1 represents some physical properties of the light hydrocarbons, which are of great importance for the separation of their mixture.

Methane is applied for heat and electricity generation and in transportation. One of the most practical applications of methane is chemical conversion of methane specifically syngas to other chemicals such as methanol [2-4]. Separation and purification of the methane and other light hydrocarbons is an essential step before each of these

applications [5,6]. C_2 hydrocarbon recovery is economically favorable since C_2 hydrocarbons are utilized in production of rubber and plastics [2,7]. Figure 1 illustrates the increasing trend in number of publications on the light hydrocarbon separation. The top 10 countries with the highest number of publications on the separation of LHs are shown in Figure 2.

Several techniques have been introduced for light hydrocarbon separations such as adsorption, cryogenic distillation, extractive distillation, membrane separation, in which some of them are leading industrial technologies and commercially, stablished such as cryogenic distillation and extractive distillation [1,8-10]. To remove and reduce the quantities of impurities and nonhydrocarbon compounds from the refinery gas, several purification techniques such as washing, compression and drying are performed to obtain a purified stream of light hydrocarbons with high efficiency in the subsequent processes.

Table 1. Physical properties of light hydrocarbons of C_1, C_2, and C_3

Component	Boiling point (K)	Kinetic diameter (Å)	Dipole moment ($\times 10^{18}$ esu cm)	Quadrupole moment	Polarizability ($\times 10^{-25}$ cm^3)
CH_4	111.6	3.758	0	0	25.93
C_2H_6	184.55	4.443	0	0.65	44.3
C_2H_4	169.42	4.163	0	1.50	42.52
C_2H_2	188.40	3.300	0	-	33.3
C_3H_8	231.02	4.300	0.084	-	62.9
C_3H_6	225.46	4.678	0.366	-	62.9

Figure 1. Number of publications on light hydrocarbon separation from 1970 to July 2020 based on Scopus database (www.scopus.com)
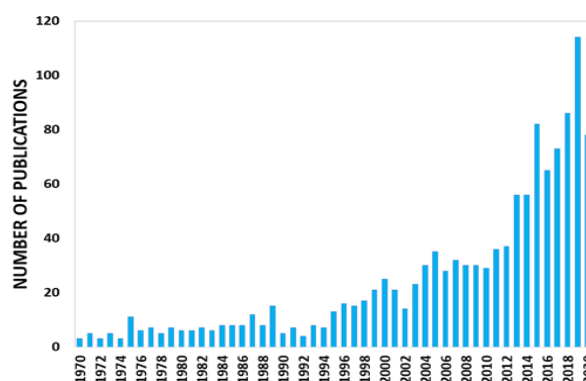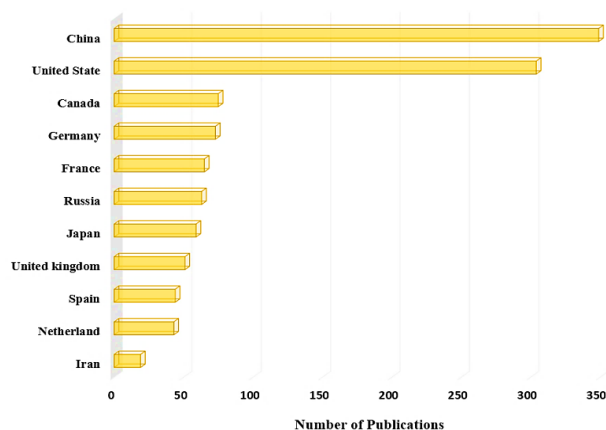
Figure 2. Top ten countries with the highest number of publications on light hydrocarbon separation during 1970 to July 2020 based on Scopus database (www.scops .com)
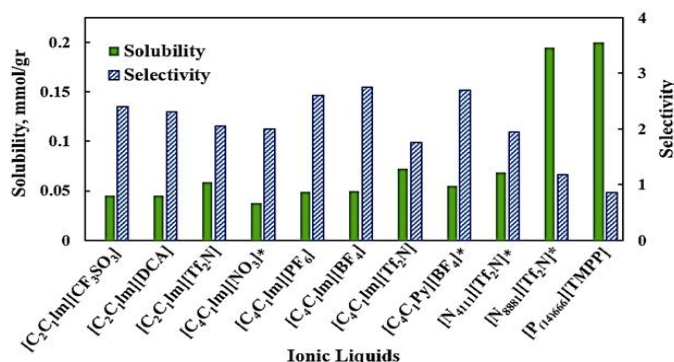

Distillation and absorption are the two major industrial methods for light hydrocarbons separation. However, both of them have low economic efficiency because of high-energy consumption and installation cost. Adsorption using porous adsorbents such as porous carbons, Zeolites, and metal organic frameworks (MOFs) are considered as promising method for the light hydrocarbon separation and purification due to the recyclability, energy efficiency and ecofriendly characters of the solid and porous materials [11-15]. However, it needs more investigations to find an energy saving solid-state adsorbent with high selectivity and separation efficiency. For selective separation of C_2H_6/CH_4 and C_3H_8/CH_4 mixtures, porous structures with uniform micro-porosity are desired due to the kinetic diameter of light hydrocarbons that is in the range of 3.75-5.12 Å. In this review, we discussed some commonly used industrial methods for separation of the light hydrocarbons and highlighted the recent advances in separation techniques using porous adsorbents and membranes specially using metal organic frameworks.

Separation of LHs using cryogenic distillation

Cryogenic distillation and extractive distillation are the leading industrial processes for the separation of light hydrocarbon separations [1-4,8-10]. Liquefied natural gas (LNG) as a green fuel is a cryogenic liquid of 111 K at atmospheric environment with high energy density and environmentally favorable advantages that need to be vaporized at the destination application. Vaporization at the destination application results in the releasing of the large amount of cold energy, which could be recoverable and has economic benefits [1,5]. Cryogenic separation of light hydrocarbons requires several compressor power coupled with the refrigeration system; however, light hydrocarbon separation from the refinery gas can be utilized using the low refrigeration-compression systems [1,5]. This process includes a predistillation tower, two demethanizer, an ethylene fractionator, a depropanizer, and a debutanizer. Predistillation tower separates the C_1 from C_2^+ hydrocarbons. The top product goes over first demethanizer as four different feed streams and the bottom product goes over the second. Ethylene and heavier hydrocarbons are separated from lighter ones in first demethanizer and the top gaseous product is compressed and condensed to about 4 MPa and 166 K. The condensed stream are separated to two liquid and vapor streams using a Flash column. The vapor stream goes over the refrigeration system and the liquid stream reflux into the top of first demethanizer. To separate the

heavier hydrocarbons, the bottom product of first demethanizer flows to the second demethanizer, ethylene fractionator, depropanizer, and debutanizer, respectively [1].

Separation of LHs using extractive distillation

Cryogenic distillation typically uses a huge amount of energy and extractive distillation typically requires a volatile organic extracting compound, while high volatility results in the loss of solvent and environmental contaminants. Using a highly stable and green extracting agent with low volatility and high solubility for light hydrocarbons may address this issue.

Ionic liquids (ILs) is a proper candidate for extractive distillation of light hydrocarbons because of their unique physicochemical properties such as high thermal stability, low volatility, tunable structure by varying cations and anions [16-19]. Paraffin with different carbon numbers can be soluble in various ionic liquids [20-22]. Dean Camper *et al.* [23] evaluated the solubility of hydrocarbons such as ethane, ethene, propane, propene, isobutane, butane, 1-butene, and 1,3-butadiene at room temperature ILs with imidazolium rings such as [bmim][PF$_6$], [bmim][BF$_4$] and [emim][CF$_3$SO$_3$], at low pressures. The results revealed an increment in the solubility by

increasing the carbon number in ILs and double bound in hydrocarbon.

Figure 3 indicates the selective solubility of C_3H_8 compared with CH_4 and C_2H_6 by different ILs. As shown in Figure 3, among imidazolium ILs, $[C_6C_1Im][Tf_2N]$ shows the highest solubility of 0.006, 0.026 and 0.083 mmol. g^{-1} for CH_4, C_2H_6 and C_3H_8 at 313 K and 100 kPa, respectively. $[C_4C_1Im][Tf_2N]$ exhibits the best selectivity of 14.2 and 405 for C_3H_8/CH_4 and C_2H_6/CH_4 respectively. By increasing the number of carbons of the alkyl side chains in ILs due to the stronger intermolecular interactions between gases and ILs molecules, the solubility of light hydrocarbons improves [24].

Both cations and onions in ILs affect the solubility of paraffin and olefin. Figure 4 illustrates the solubility of C_3H_6 and selectivity for C_3H_6 to C_3H_8 using various ILs. As shown in Figure 4, the solubility of C_3H_6 increases in the order of $[C_2C_1Im][Tf_2N] > [C_2C_1Im][DCA] > [C_2C_1Im][CF_3SO_3]$ [11]. Anion $[BF_4]^-$ also exhibits absorption capacity and selectivity for C_3H_6 compared with those of $[PF_6]$ and $[NO_3]$ anions. Marcos Fallanza et al. applied a conductor-like screening model for real solvents (COSMORS) method for developing a strategy for the selection of adequate ILs and silver salt for the selective separation of propane/propylene gas mixture [25].

Figure 3. Selective solidity of C_3H_8 compared with CH4 and C2H6 in the ILs at 313 K [6-18]

Figure 4. Mass solubility of C_3H_6 and selectivity of C_3H_6/C_3H_8 in ILs at 313 K (* at 308 K) [11,15, 16,19-21]

Generally, more electron donor nature of anions results in the higher solubility of light hydrocarbons, while such anions showed lower selectivity for propane/propylene. Large anions such as BF$_4^-$ with disperse charge have smaller solubility and higher selectivity for propane/propylene at same time [16, 25].

Separation of LHs using zeolites and porous carbons

Zeolites as microporous crystalline solid materials are promising candidates for selective gas adsorption. Molecular sieve nature and electronically charged structures makes them a proper adsorbent for separation of the gaseous mixtures especially light hydrocarbon separation [22,24,26-31].

Sonja Schmittmann *et al.* [30], studied adsorption of light hydrocarbons on zeolite 13X for temperatures ranging from -80 °C to +20 °C and partial pressures of 5-1250 Pa. The results revealed that lower temperature effectively increased the selectivity of alkane-alkene separation. Yang *et al.* [31] synthesized Y zeolite with different ions such as Na, K, Li, and Ca and studied propane separation using these zeolites with different ion exchange degree from 0-94%. As can be seen in Figure 5, the slope of propane breakthrough curves for different adsorbents reflects adsorption capacity and rate.

As shown in Figure 6, Yang *et al.* [31] also synthesized 5A type zeolite with a specific surface area of 520 m²gr⁻¹ with an adsorption capacity of 8.1 wt% for C_3H_8 with a molecular size of 4.9 Å. While 3A and 4A zeolites with very low surface area and effective window size smaller than propane size showed a very poor adsorption since propane could not access the pores. However, 3A, 4A and 5A zeolites showed proper potential for ethane adsorption with adsorption capacity of 0.08, 1.2, 2.78 wt%, respectively. 4A zeolite exhibited a steady breakthrough that reveals lower adsorption rate of ethane on small pores of this zeolite compared with 5A zeolite [31].

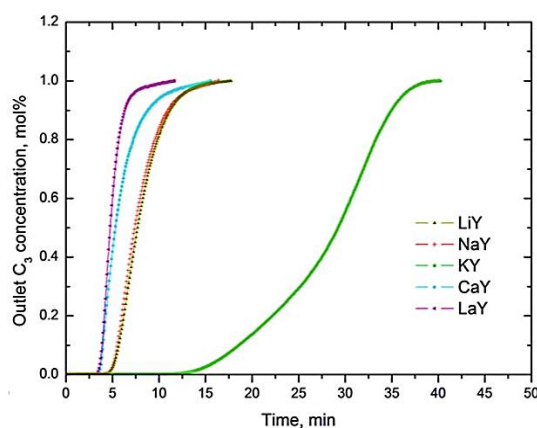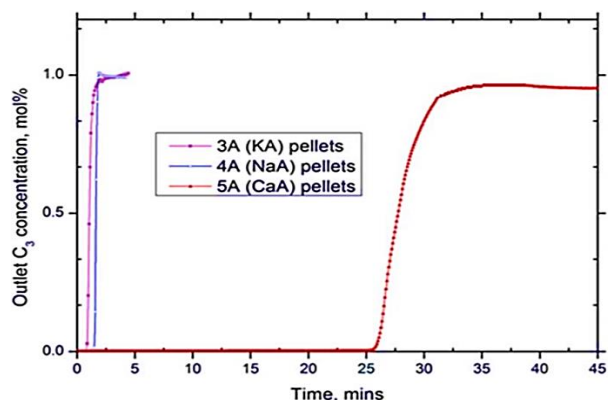**Figure 5.** Propane breakthrough results for Y zeolites [31]

Figure 6. C_3H_8 breakthrough results for A zeolites [31]

Porous carbons are promising materials for gas adsorption due to low cost, high adsorption capacity and low moisture adsorption [32-35]. Due to the smaller size and non-polarity of methane compared with the other light hydrocarbons, adsorptive separation of CH_4 is easier; however because of similar molecular size, the separations of C_2H_2/C_2H_4, C_2H_4/C_2H_6 and C_3H_6/C_3H_8 are extremely challenging [35,36]. Wang *et al.,* reported an enhanced adsorption capacity of microporous carbons with high specific surface area for $C_3/C_2/C_1$ separation at 298 K and 1 bar with the high selectivity of 65.7 and 501.9 for C_2/C_1 and C_3/C_1, respectively [36]. Using DFT simulation, shown in Figure 7, the adsorption energy of CH_4 on S-graphene is smaller compared with other light hydrocarbons. Adsorption energy difference for CH_4/C_3H_6 and CH_4/C_3H_8 mixtures are highly significant. The results revealed more strong interactions between S-graphene with C_2 and C_3 hydrocarbons in comparison with CH_4, which is consistent with the Grand Canonical Monte Carlo (GCMC) results [37].

Sonja Schmittmann *et al.* [30] studied the adsorption of light hydrocarbons on activated carbon for temperatures ranging from -80 °C to +20 °C and the partial pressures of 5-1250 Pa. The adsorption results revealed an increased curvature of adsorption isotherm by decreasing the temperature. Large isotherm slop at lower temperatures than high temperatures emphasized the occupation of adsorption sites at low partial pressures. Adsorption capacities showed an increment with decreasing temperature, due to the occupation of adsorption sites, which are less energetically valuable.

Selective separation of LHs Using Metal Organic Frameworks

Metal-organic frameworks (MOFs) are a promising class of crystalline porous materials developed in many research fields over the past few decades. They are formed *via* connection of metal ions or metal clusters through coordination bonds with organic moieties as linkers to give a low density, high specific surface area, highly porous and flexible ordered frameworks. MOFs have been favorable to many applications such as adsorption and separation of gases [38], heterogeneous catalysts [39], drug delivery [40] and bio- and gas-sensing [41]. Based on the type of ligand group, various structures of Metal-Ligand are synthesized. The most common types of organic ligands in MOFs are nitrogen-donor [42], oxygen-donor, and hetero-functional ligands [42]. Different synthesis methods are applied for MOF's synthesis such as solvothermal [43,44], mechanochemical [45], electrochemical [46] and supercritical [47] methods.

Figure 7. Adsorption energies for CH_4/C_2H_2, CH_4/C_2H_4, CH_4/C_2H_6, CH_4/C_3H_6, and CH_4/C_3H_8 mixtures on S-graphene surface [36]
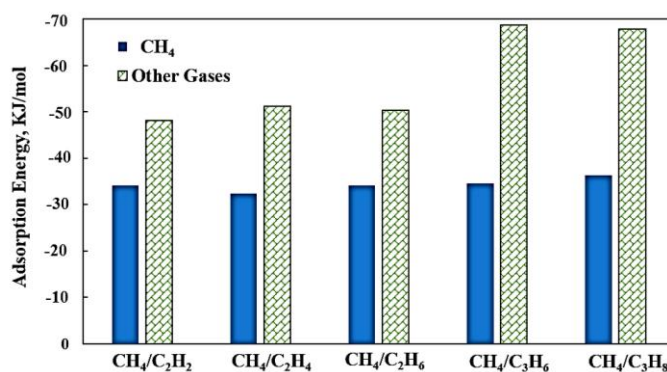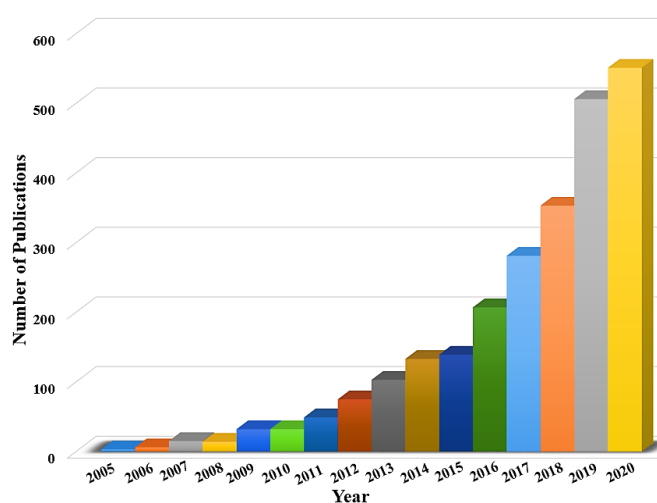
Figure 8. Publications related to hydrocarbon separation using metal organic frameworks since 2005 (www.sciencedirect.com, key words: hydrocarbon separation, MOFs)

The solvothermal method as the most common synthesize rout, includes the reaction of the metal salt and the organic ligand in the presence of solvent typically comprising formamide [43,44], alcohols [48], or pyrrolidone [49] at a temperature depending on the solvent boiling point, usually less than 523K, with a synthesis yield of 60-90%. Solvent removal from the MOF's pores is an important and sensitive method that usually takes several days.

Metal organic frameworks (MOFs) as a highly porous crystalline structure are promising material for the separation of light hydrocarbons in recent years. Figure 8 shows the number of publications related to hydrocarbon separation using MOFs since 2005. Their high porosity, surface area and tunable structure have made them potential choices for gas adsorption [50,51].

Many studies have examined the adsorptive separation of light hydrocarbon mixtures using MOFs, leading to significant improvements in key properties such as capacity and selectivity. Several MOFs such as ZIF-7 [$Zn(bim)_2$, bim^- = benzimidazolate] [52] are reported for the separation of light olefin/paraffin mixtures such as ethylene/ethane via selective gate-opening mechanism. ZIF-7 exhibited a Type IV adsorption isotherm at ambient temperatures for both ethylene and ethane [52, 53]. The results revealed a more exothermic adsorption for ethane than ethylene at all pressures and proved that the gate opening mechanism occurs more readily for the alkanes. Moreover, ethane has maximum van der Waals interactions with ZIF-7 pores due to its threefold rotational symmetry [52]. CPL-1 [$Cu_2(pzdc)_2(pz)$; $pzdc^{2-}$=2,3-pyrazinedicarbonxylane] exhibited a sharp

step in its ethylene adsorption isotherm at 273 K and 2 bar, while no step is seen for ethane at same condition even at high pressure of 10 bar [54]. The breakthrough results demonstrated successful separation of equimolar ethylene/ethane mixtures at 8 bar and 273 K using CPL-1. The CPL-1 also selectively adsorbed propylene over propane by gate opening process and showed capability to separate mixtures of these hydrocarbons at 273 K [55]. Eric D. Bloch *et al.* [56] studied a MOF termed Fe_2 (dobdc) (dobdc4–:2,5-dioxido-1,4-benzenedicarboxylate) for selective separation of ethylene/ethane and propylene/propane mixtures at 318 K. The selective separation of the synthesized MOF with open Fe^{2+} coordination sites was related to the side-on coordination of olefins at Fe^{2+} centers. Ting Chen *et al.* [57] synthesized a MOF termed FJU-99 using the V-shaped bidentate ligand with a specific surface area of 802.5 $m^2.g^{-1}$ for separation of acetylene-containing mixtures. The modified FJU-99 membrane exhibited a high selectivity for C_2H_2/CH_4 and C_2H_2/CO_2 mixtures at 296 K.

Xiu-Yuan Li [58] synthesized a strontium-MOF with polar tubular channels using $SrCl_2.6H_2O$ and oxalamide-containing ligand as a selective adsorbent for equimolar C_2H_6/CH_4 mixture separation. As shown in Figure 9, the adsorption selectivities for equimolar C_2H_6/CH_4 mixture at 298 and 333 K was 22.5

and 17.5, respectively, at atmospheric pressure.

Zeolitic Imidazolate Frameworks (ZIFs) are the crystalline porous structures composed of transition-metal ions connected to imidazole ligands similar to Si–O bond in zeolites [59]. Due to the similarity in the metal-imidazole-metal angle to the Si-O-Si, *i.e.* 145∘, ZIFs has a zeolite-like topology with an aperture sizes mostly in the range of 3 to 5 Å that makes them highly selective for light hydrocarbon mixtures. These structures show high thermal stability and superior chemical stability and are categorized as metal organic frameworks [59,60]. Siheng Qian *et al.* [61] reported preparation of a selective mixed-matrix membrane consisting polyionic liquid (PILs) and anion-pillared microporous materials for acetylene/ethylene mixture with the separation selectivity of 112. To improve the compatibility between polymer chain and MOFs structure, ionic polymers were applied to increase electrostatic interactions between polymer chains and anion-pillared resulted in defect-free MMMs. Eduardo Andres-Garcia *et al.* [62] studied adsorptive separation of propylene/propane mixture using sodalite ZIF-8 frameworks with various cations in the framework including ZIF-8(Zn), ZIF-8(Co) and ZIF-8(Fe). Various cations affect the flexibility of the ZIF-8 framework and the selectivity of gas mixture.
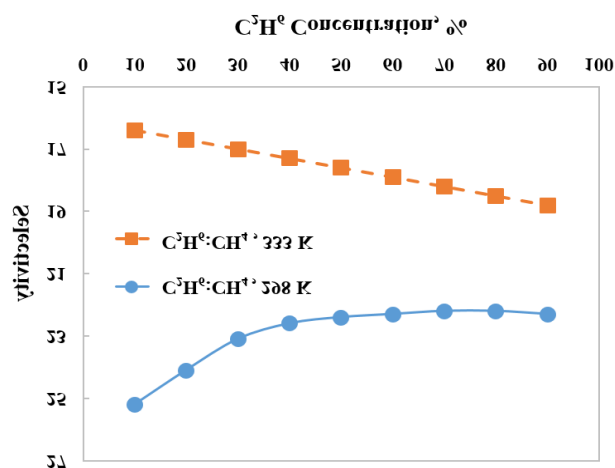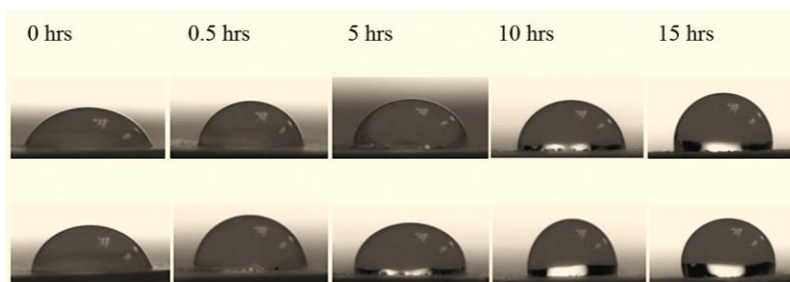
Figure 9. Adsorption selectivity of $C_2H_6:CH_4$ mixture using a strontium-MOF at different temperatures with the concentration of C_2H_6 [58]

Figure 10. Change in the contact angle of ZIF-8 membranes by MSLER time at 60 ◦C (top) and 75 ◦C (bottom) [65]

ZIF-8(Co) and ZIF-8(Fe) showed a selective separation toward propane and propylene, respectively. Weidong Fan *et al.* [63] improved the C_3H_6/C_2H_4 separation efficiency through pore engineering using different functional groups in ligands of a Microporous Cu-MOF.

Yichang Pan *et al.* [64] developed a ZIF-8 membrane for propylene/propane separation with a separation factor of 90 through the optimization of the framework activation process. Joshua B. James et al [65] modified a ZIF-8 membrane *via* the method of surface ligand exchange using dimethylbenzimidazole (DBIM) and the modified membrane exhibited increases of 40-70% in propylene/propane selectivity with a propylene permeance loss of about 10-20%. Applying surface ligand exchange resulted in a change in the hydrophilicity of the ZIF-8 membrane surface as shown in Figure 10. Depending on the duration of ligand exchange reaction, separation factor for propylene/propane can be enhanced. At short modification time of 30 min, the modified pore size greatly hindered propane diffusion without a significant effect on propylene diffusion, while long modification time exhibited an adverse effect on the propylene/propane selectivity.

Some of the most investigated mechanisms for the LHs separation using MOFs include molecular sieving, gate opening, kinetic-driven, and thermodynamic equilibrium driven mechanism.

Conclusions

This review summarized different methods utilized for light hydrocarbon separation industrially and experimentally. Cryogenic and absorption methods are the industrial processes usually utilize for natural gas purification. Research studies have shown that porous solid adsorbents such as porous carbons, zeolites and metal organic frameworks can be effectively separate heavier hydrocarbons from methane even at mild operation conditions. The adsorption kinetics of the LHs on the porous framework and microstructure of adsorbent including specific surface area, framework flexibility, pore volume, pore diameter, functional groups, and framework charge are critical parameters to select a proper adsorbent for a selective separation of LHs mixtures. Among the reported adsorbents, metal organic frameworks are the promising materials for selective separation of LHs because of their tunable framework with functional groups as well as high specific surface area. Accordingly, a rapid progress in the hydrocarbon separation using MOFs has been made in last decade. Some of the most investigated mechanisms for the LHs separation using MOFs include molecular sieving, gate opening, kinetic-driven, and thermodynamic equilibrium driven mechanism. Design and synthesis of a multifunctional MOF with cooperative separation mechanisms is essential for a high performance separation. Along the all unique properties of the MOFs as adsorbents

or membranes, there are still some issues need to be improved or addressed as follows:

- Improving the thermal and mechanical stability of MOFs,
- Precise control over pore size, pore shape, and framework charge of MOFs to develop a multifunctional MOF,
- Developing MOFs-based composite materials to enhance the separation selectivity through synergetic effects of two or more functional material in one adsorbent or membrane structure.

Disclosure statement

No potential conflict of interest was reported by the authors.

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