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Ionic liquids as entrainers for the separation of aromatic–aliphatic hydrocarbon mixtures by extractive distillation

Ismael Díaz [a,*], José Palomar [b], Manuel Rodríguez [a], Juan de Riva [b], Víctor Ferro [b], Emilio J. González [a]

[a] Departamento de Ingeniería Química Industrial y del Medio Ambiente, ETS Ingenieros Industriales, Universidad Politécnica de Madrid, 28006 Madrid, Spain
[b] Sección de Ingeniería Química, Universidad Autónoma de Madrid, 28049 Madrid, Spain

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ABSTRACT

The conceptual engineering of a new process proposed for the aromatic–aliphatic separation from naphtha has been developed based on extractive distillation using the 1-ethyl-3-methyl imidazolium dycianamide [EMIM][DCA] ionic liquid as entrainer. Process designs and simulations have been carried out with a computer-aided methodology recently developed in our group that integrates molecular modeling and process simulation via COSMO-based thermodynamic models in Aspen Plus. The computational analysis has been performed for two different multicomponent real-like naphtha models: a low aromatic content naphtha (10 wt%) and a naphtha with a high aromatic content (90 wt%). A sensitivity analysis with 8200 different extractive distillation column designs has been carried out varying the ionic liquid solvent to feed ratio, reflux ratio, number of stages and feed stage, in order to optimize the column design minimizing the reboiler duty and maximizing the throughput. In the low aromatic content naphtha, the results show that similar separation efficiencies to liquid–liquid extraction may be achieved by extractive distillation, requiring lower solvent to feed ratios but higher energy consumptions. For the high aromatic content naphtha, good separation performance is obtained with a significant reduction of the energy required per ton of naphtha fed to the system in comparison with the separation by liquid–liquid extraction. To evaluate the behavior of the process simulator using COSMOSAC, the classical NRTL thermodynamic model, fitted using experimental vapor–liquid and liquid–liquid data, was used to simulate the extractive distillation process for a simpler binary n-heptane–toluene mixture. Similar results are obtained using COSMOSAC and NRTL models for this binary aromatic–aliphatic mixture indicating the reliability of the COSMOSAC-based simulations of more complex multicomponent naphtha separation.

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1. Introduction

Separation of aromatic hydrocarbons from naphtha has a great interest for the petrochemical industry (Asselin, 1977; Choi et al., 2002; Meindersma and de Haan, 2008a). On one side, aromatic hydrocarbons represent an extra load for the naphtha crackers, negatively affecting the process economy as additional operative and capital costs. On other side, aromatic hydrocarbons have their own value as raw materials, being further transformed in higher value-added products.

Several technologies have been developed for separating aromatic hydrocarbons from aliphatic ones, mainly depending on the aromatic content of the naphtha mixture. It is commonly accepted (Meindersma and de Haan, 2008a) that separation processes based on liquid–liquid extraction are suitable for the range of 20–65 wt% aromatic content, extractive distillation for naphtha with an aromatic content of 65–90 wt% and azeotropic distillation for higher aromatic content naphtha (>90 wt%). However, it is also frequent to find naphtha with aromatic contents lower than 20 wt%. This low concentration range represents a technological challenge for the petrochemical industry, but has received a relative limited attention.

The development of new technologies for the aromatic separation from aliphatic hydrocarbons present in naphtha implies necessarily an adequate solvent for the separation process used. A number of organic compounds (usually polar species) have been evaluated as solvents in these processes (Meindersma and de Haan, 2008a): sulfolane, N-methyl pyrrolidine, N-formyl morpholine, ethylene glycols or propylene carbonate. All in all, sulfolane has resulted the most extensively used thanks to an UOP technology, which employs it as extracting solvent. In this process, sulfolane has to be recovered from both the extract and the raffinate after liquid–liquid extraction, which entails high investment and energy costs (Choi et al., 2002). Ionic liquids (ILs) are a novel attractive candidate for this separation since Seddon in 1997 (Seddon, 1997) reported the great capacity of imidazolium ionic liquids to dissolve benzene. Subsequently, large number of ILs of different families (imidazolium, pyridinium, pyrrolidinium, ammonium, etc.) have been experimentally evaluated as solvent for liquid–liquid extraction of benzene, toluene, ethylbenzene or xylene from their binary mixtures with aliphatic hydrocarbons (Requejo et al., 2016; Larriba et al., 2014b,c,d; Sakal et al., 2014; Dominguez et al., 2014a, 2011; Manohar et al., 2013; Gonzalez et al., 2013, 2010, 2009; Garcia et al., 2013, 2012, 2011, 2010a,b; Fandary et al., 2012; Kamankesh et al., 2012; Al-Tuwaim et al., 2012; Kareem et al., 2012; Maduro and Aznar, 2010, 2008; Hansmeier et al., 2010; Pereiro and Rodríguez, 2010; Arce et al., 2008a,b; Domanska et al., 2007b,a; Meindersma et al., 2006a,b; Letcher et al., 2005; Letcher and Deenadayalu, 2003; Selvan et al., 2000). In contrast, the vapor–liquid equilibria information of the aromatic + aliphatic + ILs systems, needed to properly design the IL regeneration (usually proposed to be carried out by flash distillation), have been by far less studied (Kato and Gmehling, 2005a,b; Kato et al., 2004; Navarro et al., 2016a,b, 2015; González et al., 2015). These studies have been mainly centered in thermodynamic criteria related to the corresponding operations, whereas, unfortunately, techno-economic considerations have been noticeably less taken into account. On the other hand, the development a new processes to separate aromatic hydrocarbons from naphtha with ILs has been limited until now due to the lack of thermodynamic, kinetic and transport property data of multicomponent naphtha + IL systems, required information to proceed with the design of both the individual operations and the overall process. Thus, the existing experimental information for those systems is mainly restricted to binary aromatic–aliphatic mixtures, so the extrapolation to real naphtha requires of some simplifications in order to describe multicomponent phase equilibria data. In addition, the great amount of possible existing ILs (>300 commercial and >10^6 synthesizable compounds) – whose solvent performance is determined by both cationic and anionic features – certainly limits the scope of the experimental screenings to design ILs with optimized properties for

extracting aromatic hydrocarbons from naphtha. As a result, the first conceptual design of the process for the aromatic separation from naphtha using ILs is relatively recent (2008) (Meindersma and de Haan, 2008a). This development was centered in a very low aromatic content naphtha (around 10 wt%), using liquid–liquid extraction. This work was limited to the extractive operation and it explicitly omitted modeling the vacuum distillation, operation proposed to regenerate the IL. The authors justified this decision due to the absence, in that moment, of sufficient thermodynamic data conveniently elaborated to simulate the corresponding VL separation with commercial process simulators such as Aspen Plus.

Recently, we have successfully applied a simulation strategy for performing the conceptual design of both the individual operations (Ferro et al., 2015) and the complete process (de Riva et al., 2016) to separate aromatic hydrocarbons from low-aromatic content naphtha by liquid–liquid extraction using ILs. Our process development included the proposal and techno-economical evaluation of different process configurations to, efficiently, separate aromatic products and to regenerate the IL. A main contribution of these works was the incorporation of multicomponent mixtures to model the naphtha in the process simulations. This result was possible because of the consistent application of a computational methodology that combines the molecular modeling and the process simulation supported by the COSMO-based thermodynamic models (Ferro et al., 2012a). The COnductor-like Screening Model for Real Solvents (COSMO-RS) (Klamt, 1995), derived from quantum chemical COSMO theory (Klamt and Schuurmann, 1993), predicts thermodynamic data of fluid mixtures using molecular information of the individual components. COSMO-RS have shown very good results in the prediction of liquid–liquid equilibria of ternary mixtures aromatics + aliphatics + IL (Dominguez et al., 2014b; Kurnia et al., 2013; Shah and Yadav, 2012; Ferreira et al., 2012; Palomar et al., 2009; Hansmeier et al., 2007). In addition, some commercial flowsheeting simulation software, such as Aspen Plus, have introduced a property package where activity coefficients are computed using COSMO based models, such as COSMO-RS or COSMO-SAC (Lin and Sandler, 2002). The successful integration of predictive thermodynamic models, like COSMO-based ones, into the property system of Aspen Plus and Aspen HYSYS allow fruitfully overtaking the lack of information of naphtha-ILs mixtures. This multiscale computational strategy has demonstrated excellent to be an excellent tool capable of dealing with processes and operations involving ILs and their mixtures with gases and organic molecular solvents (Ferro et al., 2012a,b; Bedia et al., 2013; Ruiz et al., 2014). Recent studies (Ferro et al., 2015; de Riva et al., 2016) demonstrated that liquid–liquid extraction with ILs is a valid technological option to separate aromatic hydrocarbons from low-aromatic content (up to 10 wt%) naphtha under technical and economic criteria.

In this work, the multiscale computational methodology is applied to the conceptual design of a new process based on an extractive distillation column (EDC) to separate aromatic hydrocarbons from naphtha, using an IL as entrainer. The suitability of the extractive distillation technology for separating aromatic compounds from naphtha was evaluated for two multicomponent aliphatic–aromatic mixtures: a naphtha with low aromatic content (10 wt%) and a naphtha with high aromatic content (90 wt%). The solvent 1-ethyl-3-methylimidazolium dycianamide ([EMIM][DCA]) was selected as entrainer in the EDC because its great influence over the relative volatility of aromatics–aliphatics mixtures (Navarro