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Synthesis of dibasic esters: A review

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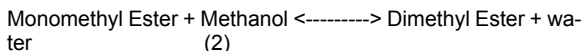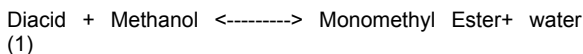
ABSTRACT

Dibasic esters (DBEs) are valuable chemical compounds that have varieties of applications industrially and they are considered as environmentally friendly (green) solvents used mostly as paint strippers. Production of DBEs have been studied over the last few decades which has certain challenges that are still being investigated in order to make the production economical. This review article introduces DBE compounds and highlights all the studies that have been done so far for the synthesis of dibasic esters along with challenges and any possible future scopes.

Keywords : Dibasic esters, dicarboxylic acids, Esterification

Introduction:

Dibasic Esters (DBE), also known as DMEs (dimethyl esters), are chemical compounds composed of a mixture of three dibasic esters namely: dimethyl adipate (DMA), dimethyl glutarate(DMG) and dimethyl succinate (DMS). DBE is used in a variety of solvent applications both as a standalone solvent and in formulations; however, it can be used as a chemical intermediate. It has been considered as green solvent to replace toxic and highly volatile solvents such as methylene chloride [13]. There are six DBE blends based on different fractions of the pure esters for specialty applications (DBE-2, DBE-3, DBE-4, DBE-5, DBE-6, DBE-9). The most popular DBE blends used in paint stripping formulas contain about 90 percent DMA. Also, DBEs have applications in coating industry to clean adhesives, polyurethane foams and unsaturated polyester resins [7].

Dibasic esters are generally produced by catalytic esterification of dicarboxylic acids. Adipic acid, glutaric acid and succinic acid react with methanol in presence of an acidic catalyst (homogeneous or heterogeneous) with the following two stage cascade reactions:

Diacid + Methanol <---------> Monomethyl Ester+ water (1)

Monomethyl Ester + Methanol <---------> Dimethyl Ester + water   (2)

Since it is an equilibrium reaction, removing water from the system causes the reaction to shift towards formation of the desired product according to Le Chatelier's principle. By studying phase equilibrium, it is possible to find any potential azeotrope and figure out the best way to separate water from the system. Also, boiling range of the components is extremely important in design of process.

This article highlights a literature review on synthesis steps of diesters along with all challenges imparting the system and suggestions for retrofitting of existing processes.
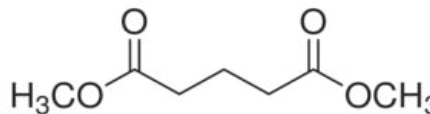
Literature Review:

DMA, DMG and DMS are the dimethyl esters of six, four and five carbon dicarboxylic acids respectively. They are very similar in structure (Figure 1) differing by just one alkyl carbon.

Dimethyl Adipate (C8H14O4)
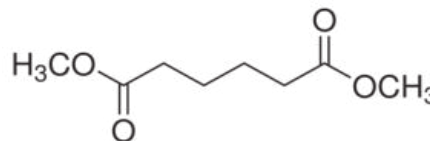
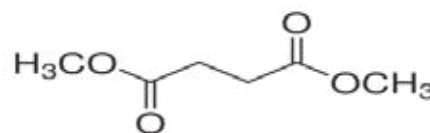Dimethyl Glutarate (C7H12O4)

Dimethyl Succinate(C6H10O4)

Figure 1: *Structure of Dibasic esters.*

DBE blend is a clear, colorless liquid, with mild odor. It is an excellent alternative to other traditional solvents because of some of its properties such as; Low (negligible) toxicity, Low vapor pressure (high boiling point), slow evaporation, high flash point, high miscibility with most organic solvents, low miscibility with water, biodegradability.

Dibasic esters are produced from esterification reaction of dicarboxylic acids of adipic, glutaric and succinic acids with methanol in presence of acidic homogeneous or heterogeneous catalysts. These valuable carboxylic acids are available in waste streams of adipic acid and caprolactam manufacturing plants which have been incinerated mostly in order to remove impurities [2]. The idea for recovery of adipic acid along with glutaric and succinic acids from the waste streams into diesters have been investigated since 1960's [8]. The process waste streams were esterified in presence of methanol in continuous reaction, extraction and distillation columns which yielded high purity of diesters [10]. The final product is a mixture of diesters which is separated from the solvent by distillation.

Use of extracting solvent introduces some disadvantages to the system such as the need for solvent recovery in the final product stream which makes the process less economical [6]. Besides, as a result of esterification of a mixture of diacids (adipic, glutaric, succinic), there is a mixture of diesters (DMA, DMG, DMS) in the product stream which have different solubility values with a particular solvent.

Introducing reactive distillation for production of DBEs via esterification has been studied to eliminate the drawbacks of the previous processes in order to obtain economical improvements to the system [4]. Hung, Lai, Huang, Lee and Yu (2008) proposed a conceptual design for reactive distillation of adipic acid and glutaric acid with methanol over solid acid catalyst and reported a high purity of diester product [5]. In this work, total annual cost is reported much higher than esterification of acetic acid because of excess use of methanol. Chan, Tsai, Lin and Lee (2009) studied a continuous esterification process of adipic acid with methanol over acidic ion exchange resin catalyst [1]. Experiments were performed in a packed column and kinetics of the reaction was evaluated at different conditions of feed mole ratio, catalyst loading and temperature. Tsai, Lin and Lee (2011) also investigated kinetics of esterification of glutaric acid with methanol over acidic ion exchange resin catalyst in a packed column in which various parameters such as: feed mole ratio, temperature and catalyst loading were studied at different values [14].

To develop a suitable reactive distillation system, a reliable phase equilibrium data are necessary. In order to shift the reaction towards formation of desired product (DMA), water needs to be removed from the reaction system. Since water is partially miscible with DMA [12] and due to formation of azeotrope between them, they are found in product stream in a liquid mixture that is separated by a decanter. Hence, liquid-liquid equilibrium of water+ DMA is useful in the design of decanter which is a key part in reactive distillation system [9]. Hung, Lin, Yu, Huang and Lee (2006) investigated LLE data of ternary system of water+ methanol+ DMA, water+ MMA+ DMA and water+ methanol+ DMG [11]. Lee, Lai, Wang and Lin (2007) obtained VLE of binary mixtures of methanol+ DMA, methanol+ DMG and DMA+ GA for which no aziotrope formation was observed [9]. There is one azeotrope recognized for the synthesis of DMA (water/DMA, 98.94/1.06 at 99.77 ˚C)[5].

Reactive distillation concept investigated so far is probably the best method for it has promising results. However, it needs modifications in order for economical improvements. One of these modifications is the use of pervaporation membrane in the RD column to remove the reaction water on site which carries several advantages [3]. By coupling of pervaporation and esterification water can be removed timely in the esterification reaction and conversion of dicarboxylic acids would increase, in addition, it would also decrease the usage of methanol, and greatly reduces the energy consumption in the process of production. Table 1 shows some of experimental studies that have been performed so far for this system.

Products	Catalyst Used	Operating Conditions	Process method	Year	Reference
DMG	Amberlyst 35	T= 40-70˚C P=1 atm	Kinetic study in packed bed column	2011	[10]
DMA	Amberlyst 35	T=40-70˚C P=1 atm	Kinetic study in Packed bed column	2010	[9]
DMA, DMG	Amberlyst 15 Amberlyst 35	T=60-190˚C P= 1 atm	Reactive distillation with decanter	2009	[7]
DMA, DMG	Acidic ion exchange resins	T=83-236˚C P=1-2 atm	Reactive distillation with decanter	2008	[8]

Table 1: **Experimental studies on DBE production**

Challenges of the system:
There are several issues accompanied with this process that must be considered and resolved. High boiling point difference between reactants, water formation and formation of azeotrope between water and diesters are issues that make the design of this esterification process challenging. Additionally, different parameters such as choice of catalyst, temperature zone in RD column, feed mole/mass ratios are crucial to attain an economical process. Since, most studies in this field deal with esterification of adipic acid, hence, challenges are explained in terms of DMA production.

Water forms an azeotrope with DMA at 99.77 ˚C and at the water to DMA ratio of 98.94/1.06 which almost corresponds to pure water. Due to this azeotrope formation, water is available at the product mixture along with DMA in batch reactor or in product stream of a continuous reactor. Separation of water from the system which causes higher yield of the diester can be further studied in order to obtain an economical process. One remedy is the use of decanter to remove water and DMA in reactive distillation system which is studied by Hung et al 2008.

Another issue that comes to the picture especially in a continuous process is that methanol and diacid have high boiling point differences. Considering the following descending normal boiling point rankings for adipic acid, glutaric acid and succinic acid esterification[5]:

AA(337.47˚C) > MMA(261.76˚C) > DMA(235.68˚C) > H2O(100˚C) > MeOH(64.53˚C)

GA(322.13˚C)> DMG(197.12˚C)> MMG(172.28˚C)> H2O (100 ˚C) > MeOH(64.35˚C)

SA(235.00˚C)> MMS (200.00˚C)> DMS(196.00˚C)> H2O (100 ˚C) > MeOH(64.35˚C)

The products of esterification reaction, DMA and water (In case of adipic acid esterification) are intermediate boilers, whereas the two reactants, methanol and adipic acid, are the lightest and the heaviest boilers respectively. Thus removal of DMA in one column is a problem which can be normally solved by introducing a combination of RD column, a decanter and a distillation column.

At the reaction temperature, methanol is completely in vapour phase while adipic acid is in liquid phase, hence the proper contact of two phases cannot be efficiently done. Additionally, adipic acid and methanol are not completely soluble at low temperatures. The solution to overcome these issues is to use large excess of methanol in the process [5] [1]. However, large methanol results in high reflux of methanol which increases cost of the process.

Future Scope
The current synthesis method for dibasic acid esters is reactive distillation technology which is undoubtedly the best technique for it makes the production continuous and economical. Also, there is a significant loss of valuable dicarboxylic acids in caprolactam plants that can be recovered to much valuable products. There are several modifications that can be investigated and implemented to the existing discussed processes.

Removal of water not only drives the reaction to completion but also facilitates column operation at relatively less feed

mole ratio of methanol to acid. Make use of a membrane inside the RD column can separate water from the system at the first stage and there would be elimination of extra decanting and distillation for water separation. However, the need for an adequate membrane is crucial that has good permeating ability and is suitable at temperature of the reaction. Additionally, there are several parameters that still need to be detected in order to make the membrane economically applicable in the system [3].

Another modification is the use of a mass separation agent (entrainer) to remove water from the RD column. This has the same advantages as the use of a pervaporation membrane. Using entrainer increases the relative volatility of water compared to alcohol, so that during the reaction water can be continuously removed by distillation. Reactive distillation with side draw can be utilised for this system since the products are intermediate boilers.

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