Tert-butanol dehydration to isobutylene via reactive distillation

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Selective tertiary-butanol (*t*BA) dehydration to isobutylene has been demonstrated using a pressurized reactive distillation unit under mild conditions, wherein the reactive distillation section includes a bed of solid acid catalyst. Feeding *t*BA to the middle of the distillation section, anhydrous isobutylene product is recovered as an overhead fraction and co-product water as a bottoms fraction. Suitable solid acid catalysts include zeolite Beta, hydrogen-fluoride-treated β-zeolites, and HF-treated montmorillonite clays. Quantitative *tert*-butanol conversions have been realized.

KEY WORDS: *tert*-butanol; dehydration; isobutylene; Beta-zeolite

1. Introduction

There has been an enormous technological interest in tertiary-butanol (*t*BA) dehydration during the past twenty years, first as a primary route to methyl *tert*-butyl ether (MTBE) [1] and more recently for the production of isooctane and polyisobutylene [2]. A number of commercializable processes have been developed for isobutylene manufacture (equation (1)) in both the USA and Japan [3,4]. These processes typically involve either vapor-phase *t*BA dehydration over a silica–alumina catalyst at 260–370 °C, or liquid-phase processing utilizing either homogeneous (sulfonic acid), or solid acid catalysis (e.g., acidic cationic resins). More recently, *t*BA dehydration has been examined using silica-supported heteropoly acids [5], montmorillonite clays [6], titanosilicates [7], as well as the use of compressed liquid water [8].

$$(CH_3)_3C{-}OH \rightarrow (CH_3)_2C{=}CH_2 + H_2O \qquad (1)$$

In an extension of our earlier studies into the use of reactive distillation for the benzene selective alkylation to make high 2-phenyl LAB's [9], we have more recently examined the potential of reactive distillation for *tert*-butanol dehydration to isobutylene using solid acid catalysis [10]. Advantages to employing reactive distillation for reaction (1) include the mild conditions required (<120 °C), quantitative *t*BA conversions per pass, and the option to use lower purity, lower cost, *t*BA feedstocks.

2. Experimental

The *tert*-butanol dehydration experiments described herein were conducted in a pilot unit reactive distillation unit of the type shown in figure 1. The unit comprises a reactive distillation column, 100, containing a bed, 102, of a *tert*-butanol dehydration catalyst, an upper distillation section, 104, containing a distillation packing (e.g., Goodloe packing) and a lower distillation section, 106, also containing distillation packing. The *tert*-butanol feedstock is charged to the middle of the bed 102 through a feed line, 110.

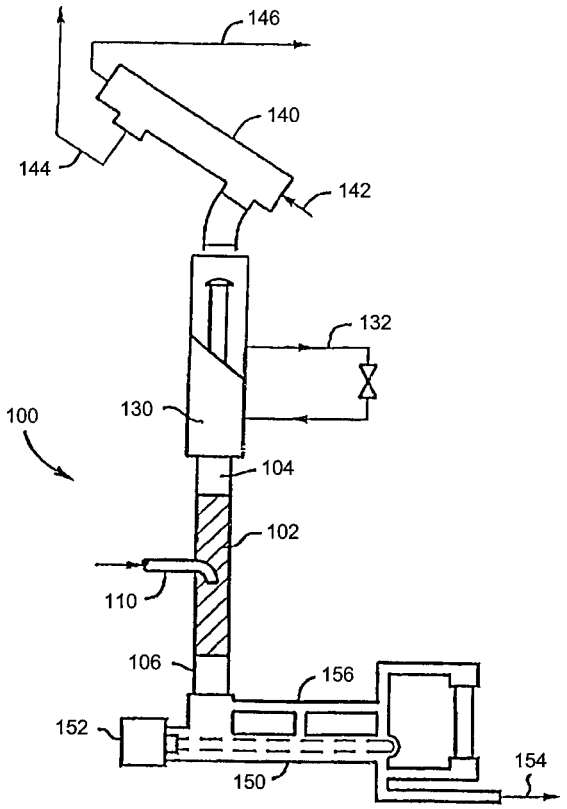

Figure 1. Reactive distillation unit design.

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The more volatile isobutylene product component flows upward through the upper distillation section 104 to a reflux splitter, 130, and then to a reflux condenser, 140, where it is cooled by room temperature water (charge line 142, discharge, 144), and withdrawn via line 146. Reflux is recirculated within the splitter 130 by a reflux line 132.

The higher boiling aqueous distillation reaction product flows downwards through the lower distillation section, 106, to a reboiler, 150, where it is heated by an electical heater, 152. A portion of the higher-boiling aqueous distillation product, 150, is withdrawn by a line 154, and the remainder of the higher boiling aqueous distillation reaction product is returned to the reactive distillation column, 100, by a reboiler return line, 156.

The Beta-zeolite catalyst samples were purchased from PQ Corporation and from UOP. The HF-treated β-zeolite and montmorillonite clay samples were prepared as described previously [9–11].

3. Results and discussion

Tert-butanol dehydration to isobutylene is an endothermic reaction (38 kJ/mol) [12] and the forward rection (equation (1)) is generally favored by high operating temperatures and low pressure [3]. However, too high a temperature (>340 °C) can lead to the formation of polyisobutylene byproducts [3]. The use of reactive distillation techniques, where the co-product water is immediately separated from the isobutylene as it is formed, allows the equilibrium of equation (1) to be shifted far to the right and high *t*BA conversions achieved under relatively mild operating conditions. Here we demonstrate quantitative *t*BA conversions to isobutylene using a pressurized reactive distillation unit (figure 1), in combination with four classes of highly active inorganic solid acid catalysts [10], namely:

- Beta-zeolites;
- HF-treated β-zeolites;
- montmorillonite clays;
- fluoride-treated clays.

Typical data for a crude (94.9%) *t*BA feedstock are illustrated in table 1. In ex. 1, 350 cm^3 of zeolite Beta having a silica-to-alumina ratio of 24 and a surface area of ca. 630 m^2/g (comprising 80% Beta and 20% alumina binder), was initially charged to the unit as 1/16″ diameter extrudates. Under steady state conditions, with the reboiler temperature set at ca. 110 °C, the column temperature 64–99 °C, and the crude *t*BA feed rate 100 cm^3/h, the overhead product fraction was found by GC analyses to comprise ca. 94% isobutylene. The corresponding bottoms product was 97% water, and included just 0.2% unreacted *tert*-butanol. The estimated *t*BA conversion is then >99%, and the isobutylene selectivity 95 mol%. Likewise, in ex. 2, charging the same Beta-zeolite composition, but operating the unit at higher feed rates (145 g/h) and using a slightly lower reboiler temperature (99 °C), *t*BA conversion is 96% under steady state

Table 1
Tert-butanol dehydration to isobutylene.

	Feed	Ex.									
		1		2		3		4		5	
Catalyst		Beta-zeolite[a]		Beta-zeolite[a]		Beta-zeolite[b]		HF/montmorillonite clay[c]		HF/Beta-zeolite[d]	
Reboiler temp. (°C)		110		99		92		127		112	
Column temp. (°C)		64–99		72–97		67–83		50–105		87–96	
Reflux temp. (°C)		50		51		46		[e]		[e]	
Reactor pressure[f] (kPa)		80		60		60		140		80	
Feed rate (g/h)		100		145		103		100		100	
		Overhead	Bottoms	Overhead	Bottoms	Overhead	Bottoms	Overhead	Bottoms	Overhead	Bottoms
Water	1.4	0.1	97.2		77.8		56.8	0.2	96.5	1.3	95.3
Methanol	0.4	0.5		0.04				0.1		0.5	
Isobutylene		94.4		93.3		76.9	0.2	80.7		59.9	
Acetone	1.4	1.6		1.7				0.9		10.7	
Isopropanol	0.3			0.04	0.5	8.4	0.9				
*t*BA	94.9		0.2	3.2	18.7	6.1	40		0.3	12.7	0.7
MTBE	0.05	2.2		1.3	0.2	6.3	0.2	5.1	1.9	10.3	1.8
Methyl ethyl ketone	0.2	0.05			1.1		0.2				
Diisobutylene	0.06	0.2	0.6	0.08	0.9	0.3	0.5	12.4	0.7	1.2	1.2
Unknowns	1.4	0.9	2	0.3	0.7	1.9	1.2	0.6	0.6	3.4	1
*t*BA conversion (%)		> 99		95.6		89.1		[e]		91.7	
Isobutylene selectivity (mol%)		94.5		88.5		67.2		[e]		64.9	

[a] From PQ Corp., 1/16″ diameter extrudates.
[b] From UOP, 1/16″ diameter extrudates.
[c] 0.6% HF on montmorillonite clay.
[d] 5.7% HF-treated Beta-zeolite.
[e] Not determined.
[f] Reactor pressure above atmospheric (101 kPa).

conditions, with 89 mol% selectivity to anhydrous isobutylene. Ex. 3–5 illustrate somewhat similar data for a second sample of zeolite Beta, as well as an HF-treated montmorillonite clay and an HF-treated Beta-zeolite catalyst. The normal column operating temperature range is generally 50–120 °C under equilibrium conditions [10].

Impurities in the crude *t*BA feed, most notably water, methanol, acetone, and "heavies", do not appear to significantly inhibit the dehydration process (equation (1)), although the presence of methanol clearly leads to the formation of additional MTBE (either through etherification of the *t*BA feedstock, or the isobutylene co-product [11]).

In summary, complete *t*BA conversion levels (>99%) have been achieved in this work using reactive distillation technology (figure 1) at significantly lower temperatures (50–120 °C) than are normally necessary using plug-flow, fixed-bed, reactors (PFR, 300 °C [3,7]) or CSTR configurations. Substantially anhydrous isobutylene is thereby separated from the aqueous co-product, as a lighter distillation fraction. Even employing crude *t*BA feedstocks, the isobutylene distillation fraction is recovered in ca. 94% purity and 95 mol% selectivity.

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