Influence of mono-hydrogenation of C5 cut on the synthesis of TAME using Amberlyst 15

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ABSTRACT. TAME was synthesized in liquid phase from refinery C5 cut and methanol using Amberlyst 15 as catalyst. The C5 stream contains mainly mono-olefins and, in a less amount, a diolefin, which have a high gum formation tendency. The main purpose of this research was to evaluate the effect of mono-hydrogenation of C5 cut on TAME synthesis. The hydrogenation step was carried out at 80 °C and 10 kgf/cm^2 of H_2, using a 0.3% Pt/Al_2O_3 catalyst. It was observed that the diolefin was totally hydrogenated and olefins content was drastically reduced without any decrease of reactive isoamylenes content. The etherification was carried out in a 250 mL stirred batch reactor at temperatures ranging 50 - 90 °C, 10 kgf/cm^2, and molar ratio of isoamylenes to methanol close to 1. Reaction products were analyzed by GC. Total conversion was similar for original and mono-hydrogenated feeds. However, the products obtained with the original cut presented foul odor and color, even at lower temperatures, characteristic of gum formation in the products. On the other hand, the product obtained from the mono-hydrogenated cut presents no foul odor and color. Therefore, mono-hydrogenation of the C5 cut is necessary to allow the addition of the produced TAME to gasoline blend.

Key words: TAME, hydrogenation, Amberlyst 15.

RESUMO. Influência da mono-hidrogenação da fração C5 na síntese do TAME usando Amberlyst 15 como catalisador. No presente trabalho, foi estudada a síntese do TAME, em fase líquida, a partir de uma fração C5 e metanol, utilizando Amberlyst 15 como catalisador. A fração C5 utilizada possui uma diolefina, que tem uma alta tendência à formação de gomas e um alto teor de mono-olefinas. Deste modo, o objetivo deste trabalho foi avaliar o efeito da mono-hidrogenação da fração C5 na síntese do TAME. A hidrogenação foi feita a 80°C e 10 kgf/cm^2 de H_2, usando um catalisador 0,3% Pt/Al_2O_3. A diolefina foi totalmente hidrogenada e o teor de mono-olefinas significativamente reduzido sem um decréscimo apreciável no teor de isoamilenos reativos. A eterificação foi feita em um reator tipo batelada de 250 mL, com agitação magnética. A temperatura foi variada na faixa de 50 a 90°C, com uma pressão de 10 kgf/cm^2 e razão molar isoamileno/metanol de aproximadamente um. Os produtos de reação foram analisados por cromatografia gasosa. A conversão total observada foi aproximadamente a mesma para o os cortes original e mono-hidrogenado. Entretanto, os produtos obtidos utilizando a fração C5 original apresentaram cheiro forte e coloração, mesmos para os testes a temperaturas mais baixas, que são características da formação de gomas. Por outro lado, quando a fração mono-hidrogenada foi usada na eterificação, o cheiro forte e coloração não foram observados. Portanto, a mono-hidrogenação da fração C5 contendo os isoamilenos reativos é necessária para que o TAME produzido na reação de eterificação possa ser adicionado à gasolina.

Palavras-chave: TAME, hidrogenação, Amberlyst 15.

Due to gasoline reformulation, there has been an increasing demand for oxygenated additives to adjust the octane number. The main oxygenated additive is the MTBE (Rabello, 1996). However, the available amount of isobutene is insufficient for the production of all oxygenates needed to reformulate gasoline. Consequently, interest in tert-amyl methyl ether (TAME) has grown steadily. TAME is synthesized by an acid catalyzed, equilibrium reaction of isoamylenes (2-methyl-1-butene and 2-methyl-2-butene) from C5 FCC stream and methanol. This oxygenate has a lower Reid vapor pressure and almost the same blending octane number than MTBE (Rock, 1992, Piccoli and Lovisi, 1995, Rabello, 1996). However, some components present in naphtha of FCC (isoamylenes source) are harmful to the catalyst in the etherification reaction. These components, mainly dienes, can polymerize forming gums that may obstruct the pores of the catalyst and reduce its useful life. Even in small amounts, gums and diolefins may also generate odor and color in the product (Rock, 1992, Piccoli and Lovisi, 1995). The usual solution to control dienes, acetylenes and gums is to selectively hydrogenate the C5 stream using hydrogenation catalysts, a noble metal (palladium or platinum) supported on an inert matrix, which should be carried out before etherification. During hydrogenation, isomerization of the non-reactive 3-methyl-1-butene to reactive 2-methyl-1-butene (2M1C4=) and 2-methyl-2-butene (2M2C4=) may also occur, leading to an increase on TAME production (Rock, 1992). The main purpose of this research was to evaluate the effect of mono-hydrogenation of a refinery C5 cut (isoamylenes source) in the synthesis of TAME on acid resin Amberlyst 15.

Material and methods

Reagents utilized were methanol (Nuclear >99.8%), C5 cut from the FCC naphtha as source of isoamylenes, and H_2 PA supplied by White Martins. A commercial acid resin, Amberlyst 15 (Rohm Haas) was used as etherification catalyst; a commercial catalyst containing 0.3% of platinum supported on alumina was selected for mono-hydrogenation of the original C5 cut.

The catalytic experiments were carried out in a stainless steel stirred batch reactor (250 mL) containing an internal stainless steel gauze basket for catalyst particles. For the hydrogenation of the original C5 cut, the reactor was loaded with 5.0 g of catalyst, closed and connected to the hydrogen cylinder. The activation was done under a flow rate of 100 mL/min of H_2 at 110 °C for 6 hours and pressure was kept constant at 5 kgf/cm^2. Moreover, approximately 100 g of the original C5 cut was fed into the reactor, at room temperature, using a piston pump, and the internal constant H_2 pressure was adjusted at 5 or 10 kgf/cm^2. Temperature of reaction was immediately raised to 50 or 80 °C. Reaction was carried out for 210 min and samples were withdrawn at regular time intervals.

For the etherification reaction, 2.0 g of resin were activated in situ at 100 °C for 6 hours under a flow rate of 100 mL/min of N_2. Approximately 100 g of a cold mixture (original or mono-hydrogenated) containing a methanol/reactive isoamylenes, molar ratio of 1.1, was fed into reactor and kept at room temperature. The pressure was then adjusted at 10 kgf/cm^2 with N_2 and reaction temperature in the range of 50 – 90 °C was immediately raised. The first sample was withdrawn before the contact with the catalyst and the other ones at regular time intervals. Reagents and reaction products were analyzed by gas chromatography using a VARIAN 3300 chromatograph equipped with flame ionization detector (FID) and capillary column DB-1 of 30m x 0.250mm x 1μm, with H_2 as carrier gas.

Results and discussion

Hydrogenation of the C5 cut

In order to optimize the hydrogenation conditions of original C5 cut, hydrogen pressure and reaction temperature were varied, as previously described. Figure 1 shows the changes in the diolefin and mono-olefins contents as a function of the hydrogenation reaction time for all runs.

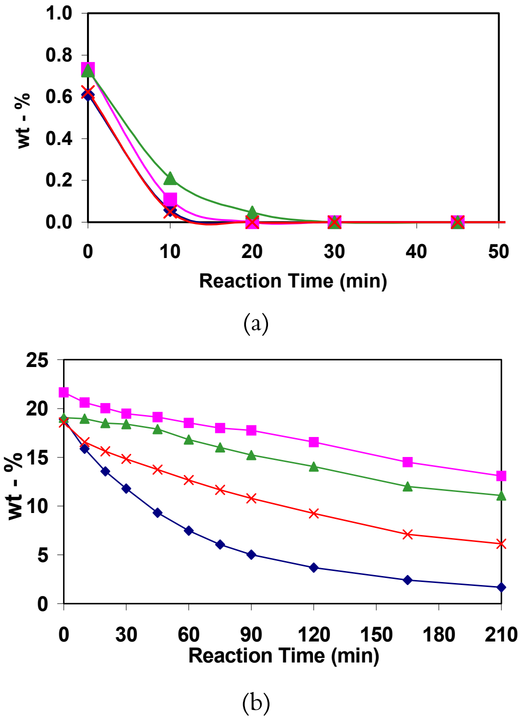
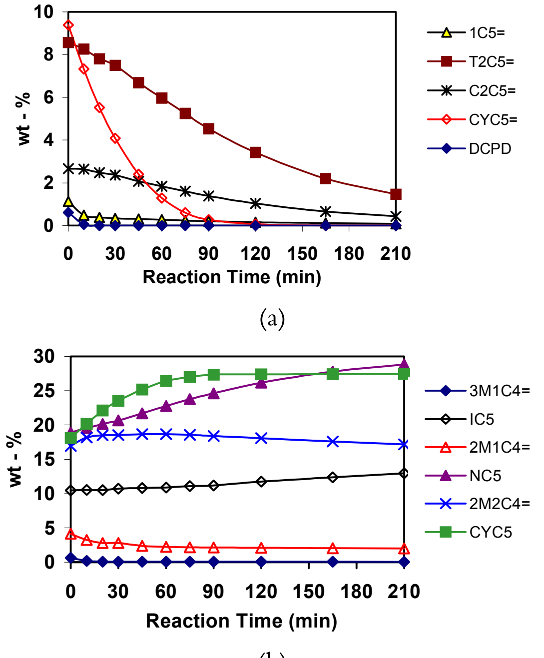


Figure 1. Change in (a) diolefin and (b) mono-olefins as a function of reaction time for the hydrogenation reaction of C5 cut at: (■) T=50°C and P_{H2}=5 kgf/cm^2; (**x**) T=50°C and P_{H2}=10 kgf/cm^2; (▲) T=80°C and P_{H2}=5 kgf/cm^2; (◆) T=80°C and P_{H2}=10 kgf/cm^2

It may be verified that the H_2 pressure influences the hydrogenation of di- and mono-olefins more significantly than the temperature of reaction. Thus, Figure 1 demonstrates that the best condition obtained to carry out the hydrogenation of original C5 cut are 80 ºC and 10 kgf/cm^2 of H_2. It may be seen that diolefin was easily hydrogenated prior to 30 min of reaction. In addition, the content of mono-olefins were strongly reduced, leading to final concentration of about 2.5 wt-% of olefins, at 210 min of reaction.

Figure 2 shows that hydrogenation in the best condition led to a significant change in C5 cut composition. There was a complete hydrogenation of the dicyclopentadiene (DCPD), main precursor of gum and foul odor (Rock, 1992, Piccoli and Lovisi, 1995). A significant decrease was also observed in mono-olefins (1C5=, T2C5=, C2C5=, CYC5=) that could polymerize and/or react with methanol, producing less important and undesirable ethers, followed by an increasing in paraffin contents.



(a)

(b)

Figure 2. Changes in the diolefin, mono-olefins and paraffins contents as a function of hydrogenation reaction time for C5 cut at 80ºC and 10 kgf/cm^2 of H_2

Figure 2 also shows that hydrogenation of mono-olefins took place without considerable loss of total reactive isoamylenes (2M1C4= and 2M2C4=), which is confirmed by the almost constant content of corresponding paraffin isopentane (IC5). Further, it may be noted that there was a decrease in the non-reactive isoamylene 3-methyl-l-butene (3M1C4=) content, probably due to hydrogenation, and also isomerization from 2M1C4= to 2M2C4=, since the content of the former decreases, whereas the content of the latter increases.

Maintaining or increasing isoamylene content in C5 cut hydrogenated is a very important point, because these compounds will be converted in TAME later. Therefore, the hydrogenation of the original C5 cut was carried out in order to obtain sufficient reagent contents for the synthesis of TAME. The final composition of the mono-hydrogenated cut, which was used in the present work besides the original one, is presented in Table 1. Final mean composition for the mono-hydrogenated C5 cut was slightly different from the one that could be obtained (Figure 2) if the hydrogenation catalyst had not decayed in the final batches.

Table 1. Final mean composition of the original and mono-hydrogenated C5 cut

Components		C_5 (wt-%)	
		Original	Hydrogenated
Paraffins		44.2	68.2
Reactive Isoamylenes	2M1C4=	4.92	2.18
	2M2C4=	17.4	19.7
Other Mono-Olefins		29.3	6.79
Diolefin	DCPD	0.946	0.00
Aromatics		1.56	1.49
Non-Identified Compounds		1.59	1.56

Synthesis of TAME on Amberlyst 15

Figure 3 shows the effect of reaction temperature on TAME synthesis using original and hydrogenated C5 cut.

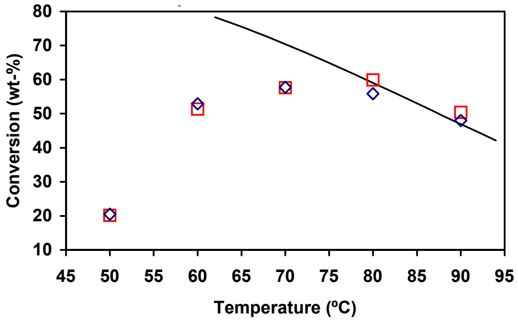
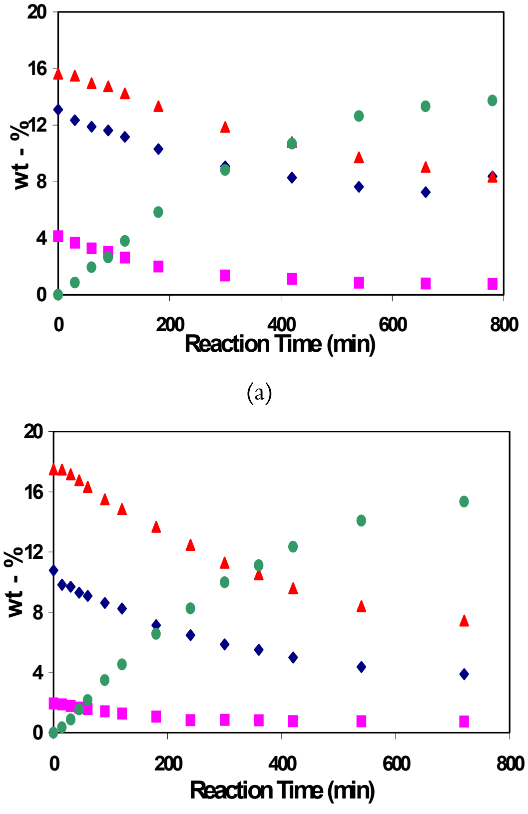


Figure 3. Total Conversion of isoamylenes as a function of temperature for C5 cut: (□) original, (◇) mono-hydrogenated, and (—) calculated thermodynamic equilibrium curve

At higher temperatures the etherification conversion declined in the same way as observed by Rihko and Krause (1996), Piccoli and Lovisi (1995) and Rihko *et al*. (1997), due to the limitation of thermodynamic equilibrium. Thus, at temperatures higher than 70 °C, as may be seen from the curve of thermodynamic equilibrium conversion, calculated using the software Aspen Plus, the reaction was significantly limited by thermodynamic equilibrium. Moreover, the equilibrium conversion for the non-hydrogenated cut was found to be slightly higher than for the hydrogenated cut at 80 °C. This could be attributed to the higher content of 2-methyl-1-butene (2M1C4=) in the original cut, which is more reactive than the 2-methyl-2-butene (2M2C4=) since, besides the etherification, the isomerization of 2M1C4= to 2M2C4= also occurs. Further, the presence of 3M1C4= that could isomerize to the reactive isoamylenes should be considered (Rock, 1992).

Figure 4 shows changes in the content of reactive isoamylenes, methanol and TAME as a function of reaction time at 70 °C. At this temperature the isoamylene conversion was high and, as discussed earlier, there was no limitation due to thermodynamic equilibrium.



(a)

(b)

Figure 4. Change in the content of reactive isoamylenes, methanol and TAME at 70 °C as a function of reaction time for C5 cut: (a) original and (b) mono-hydrogenated, where: (■) 2M1C4=; (▲) 2M2C4=; (◆) methanol; (●) TAME

At 70 °C it should be put in mind that for the hydrogenated cut the reaction time was smaller and then the conversion could still be a little higher than that observed.

Reagents and TAME showed a similar behavior in the course of reaction for both C5 cuts used, as seen in Figure 4. This behavior might indicate that the presence of inert and diolefins did not affect in a significant way the reaction products. Indeed, the isoamylene conversion and TAME selectivity, as shown in Table 2, could confirm such observation. Furthermore, the presence and content of methanol, in the conditions studied, promoted the complete solvation of the resin acid sites (Piccoli and Lovisi, 1995, Rihko *et al*., 1997), inhibiting to a large extent undesirable reactions, mainly at lower temperatures (< 80°C).

Table 2. Effect of hydrogenation of C5 cut on the isoamylenes etherification with methanol, using resin Amberlyst 15 as catalyst after 960 min of reaction

Temperature (°C)	C5 Cut	Conversion of Isoamylenes (wt-%)	TAME (wt-%)	
			Yield	Selectivity
50	Hydrogenated	20.5	18.3	89.3
	Original	20.2	17.7	87.6
60	Hydrogenated	52.9	55.1	90.0
	Original	51.9	54.0	95.9
70	Hydrogenated[♣]	57.8	54.2	93.6
	Original	57.6	53.9	93.5
80	Hydrogenated	55.9	54.7	97.8
	Original	59.9	59.7	99.7
90	Hydrogenated	47.9	47.5	99.1
	Original	50.4	53.8	106.9

[♣] After 720 min of reaction

However, in the experiments utilizing original C5 cut, a strong odor and a slightly red coloration was observed. According to Rock (1992) and Piccoli and Lovisi (1995), these are due to the presence of diolefins, mainly DCPD, and gum formation in the products, which were not detected by GC analysis. Even in small amounts these gums are highly undesirable for the blend of gasoline. On the other hand, in the synthesis using the hydrogenated C5 cut, those negative characteristics were not observed. Although the di- and mono-olefins have not influenced significantly the conversion of isoamylenes and TAME yield and selectivity, the hydrogenation of C5 cut before the etherification reaction becomes necessary to avoid color and foul odor in the reaction products.

Conclusion

The best condition obtained for C5 cut hydrogenation was 80 °C, 10 kgf/cm^2 of H_2 and 210 min reaction time. This leads to total diolefin and maximum mono-olefins conversion without loss in reactive isoamylene contents. Results obtained in the synthesis of TAME using the original and mono-hydrogenated C5 cut indicated that the best reaction temperature was at approximately 70 °C, because, in this condition, the reaction was not limited by the thermodynamic equilibrium and could reach high isoamylene conversion. Hydrogenation of C5 cut did not show any quantitative influence on isoamylene conversion and TAME yield and selectivity. However, it was observed in the synthesis using original C5 cut a slightly red coloration, and also a foul odor, characteristics of gum formation. On the other hand, in the experiments using hydrogenated C5 cut, those characteristics were not observed. It may thus be concluded that the hydrogenation of C5 cut before the reaction of etherification is necessary to avoid gum formation and foul odor, which even in small amounts may be a serious problem to the addition of the etherification products to the gasoline blend.

Acknowledgments

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Nomenclature

1C5=	1-pentene
2M1C4=	2-methyl-1-butene
2M2C4=	2-methyl-2-butene
3M1C4=	3-methyl-1-butene
C2C5=	cis-2-pentene
CYC5	cyclopentane
CYC5=	cyclopentene
DCPD	dicyclopentadiene
FCC	fluid catalytic cracking
GC	gaseous chromatography
H_2	molecular hydrogen
IC5	isopentane
MTBE	methyl tert-butyl ether
N_2	molecular nitrogen
NC5	n-pentane
T2C5=	trans-2-pentene
TAME	tert-amyl methyl ether

References

PICCOLI, R.L.; LOVISI, H.R. Kinetics and thermodynamics study of the liquid-phase etherification of isoamylenes with Methanol, *Ind. Eng. Chem. Res.*, Washington, D.C., v. 34, n. 2, p. 510, 1995.

RABELLO, C.R.K. *Modelagem matemática da síntese de Metil-Terc-Butil-Éter utilizando Amberlist-35*®. 1996. Dissertação (Mestrado em Engenharia Química) - COPPE, Universidade Federal do Rio de Janeiro, Rio de Janeiro, 1996.

RIHKO, L.K.; KRAUSE, A.O. Etherification of FCC Gasoline with Methanol, *Ind. Eng. Chem. Res.*, Washington, D.C., v. 35, n. 8, p. 2500, 1996.

RIHKO, L.K. *et al*. Kinetics model for etherification of isoamylenes with Methanol. *Ind. Eng. Chem. Res.*, Washington D.C., v. 36, n. 3, p. 614, 1997.

ROCK, K. TAME: Technology Merits, *Hydrocarbon Process.*, Houston, v. 71, n. 5, p. 86, 1992.

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