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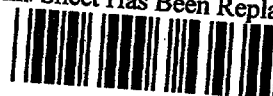
PRODUCTION OF ETHYLTOLUENE

This invention relates to a process for the production of ethyltoluene and more particularly, to a process for the production of a mixture of ethyltoluene isomers having a high content of the meta isomer and a very low quantity of the ortho isomer.

Vinyl toluene is an important industrial commodity chemical used for the production of polymers. For certain purposes, it is desirable to produce vinyl toluene with a relatively high content of the meta isomer (m-methyl styrene), typically from 50 to 70% of the total vinyl toluene content. At the same time, a very low content of the ortho isomer (o-methyl styrene) is desired since this material acts as a chain stopper in polymerization. Normally, a maximum content of the ortho isomer of 1.5% and preferably below 1 or 0.5% must be adhered to for a commercially acceptable material.

Vinyl toluene is produced from ethyltoluene by dehydrogenation with the isomer ratio of the vinyl toluene product being directly dependent upon the isomer ratio of the ethyltoluene precursor. Thus, the ethyltoluene should typically contain from 50 to 70% of the meta isomer and not more than 1% ortho isomer with the balance being made up of the para isomer.

Ethyltoluene may be produced by the ethylation of toluene in the presence of an acidic catalyst and for this purpose, Lewis acid type catalysts such as aluminum chloride as well as heterogeneous zeolite catalyst have been used. Homogenous phase Lewis acid catalysts such as aluminum trichloride are effective for the ethylation of toluene under relatively mild conditions to produce an ethyltoluene product in which the isomer ratio is relatively close to the equilibrium ratio of 31.5% para, 50.2% meta and 18.3% ortho. U. S. Patent No. 4,143,084 (Kaeding), for example, discloses (Example 13) a process



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in which toluene is ethylated in the presence of aluminum chloride to produce ethyltoluene with a p-m-o- isomer ratio of 27:60:13. While this ethyltoluene product has the requisite content of the meta isomer, the ortho isomer is present in excessive amounts.

An intermediate pore size zeolite such as ZSM-5 may be used to catalyze the ethylation of toluene, typically using temperatures in the range of 500° to 850°F (260° to 455°C). The isomer ratio of the product varies according to the specific shape selectivity characteristics of the zeolite component of the catalyst. If ZSM-5 is used in its hydrogen form without modification, the ethyltoluene product has an isomer ratio which is relatively close to equilibrium. An example of this is given in U. S. 4,086,287 where Example 3 shows that a meta content of about 60% may be obtained but that the ortho isomer is present in excessive amounts.

It is possible to modify zeolite catalysts so that selectivity for the para isomer is increased significantly above the equilibrium level. For example, by increasing the crystallite size of ZSM-5 the ratio of para to meta isomer may be raised significantly with a corresponding loss in the amount of the ortho isomer. U. S. 4,086,287 (Example 4) shows that ortho contents as low as about 1.6% may be obtained with meta contents of about 65% using a large crystal ZSM-5 catalyst. Even here however, the content of the ortho isomer is excessive. High temperatures and relatively low space velocities result in more of the meta-isomer and less of the ortho U.S. 4,086,287 (Example 4). However, higher space velocities in a commercial process are desirable because they enable more product to be produced in a unit of given size and from Example 4 there is no indication that higher space velocities will achieve the preferred isomer ratio.

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By suitable modification of the diffusion characteristics of the zeolite, the content of the ortho isomer may be reduced to suitably low levels but this is accompanied by a major increase in the selectivity to the para isomer to the extent that the process is highly regioselective. When ZSM-5 is modified with magnesium, phosphorous or boron, the content of the ortho isomer may be reduced almost to zero but in this case, selectivity for the para isomer is exceptionally high so that the ethyltoluene product does not have the desired balance of the para and meta isomer components. Processes such as this are described in U. S. Patents No. 4,086,287 and 4,143,084.

U.S. Patent No. 4,489,214 (Butler) discloses a process for producing ethyltoluene using a catalytic material described as "silicalite", a material known to be a highly siliceous form of zeolite ZSM-5. See Fyfe et al., "Resolving crystallographically distinct sites in silicalite and ZSM-5 by solid state NMR", Nature 296, 530 (1982) and Olson, D. H. et al., J. Catalysis 61, 390-396 (1980).

In summary, therefore, the problem remains of producing ethyltoluene with a relatively high content of the meta isomer and a low content of the ortho isomer not exceeding 1.5% and preferably less than 0.5%.

We have now devised a process for the production of ethyltoluene which has a relatively high content of the meta isomer and a low content of the ortho isomer. The m:p- ratio of the product is at least 1:1 (m:p-) and preferably at least 1.5:1 by weight; the level of the ortho isomer does not, in any event, exceed 1.5% and is usually below 1%. This result is achieved by suitable selection of catalyst and process constraints in the reaction.

The ethyltoluene product is produced by the ethylation of toluene in the presence of an intermediate pore size aluminosilicate zeolite catalyst of controlled

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acidity produced by steaming. The reaction is typically carried out at temperatures from 700° to 900 °F (about 370° to 480°C) with toluene:ethylene ratios from about 2:1 to 20:1 and space velocities based on the toluene feed, of about 10 to 40 (WHSV). The temperature will normally not exceed about 850°F (about 455°C).

In the present process toluene is reacted with ethylene in the presence of an intermediate pore size steamed aluminosilicate zeolite catalyst. The objective is to produce an ethyltoluene product which has a high content of the meta isomer and a very low content of the ortho isomer. The meta: para ratio of the product is at least 1:1 by weight (equivalent to at least 50 weight percent of the meta-isomer on an ortho-free basis) and is preferably at least 1.2:1 (at least 55 weight percent meta- on an ortho-free basis). In all cases, however, the maximum content of the ortho isomer is to be maintained at 1.5% and should preferably be below 1% or, better, 0.5% by weight if the ethyltoluene product is to be used for a polymerization grade vinyltoluene.

When toluene is reacted with ethylene in the presence of the shape selective heterogeneous catalyst such as ZSM-5, the initial product is probably the para-ethyltoluene which is progressively converted to the meta- and then to the ortho- isomers as contact with the acidic catalyst continues. As reaction severity increases, movement towards equilibrium is accelerated correspondingly and it therefore becomes difficult to produce a product containing relatively large amount of the meta isomer while, at the same time maintaining the content of the ortho isomer at very low levels. Normally, as shown by the Kaeding patents mentioned above, production of the meta isomer is accompanied by increasing amount of the ortho isomer as the composition of the reaction product moves toward equilibrium in the presence of the catalyst unless the shape selectivity of the catalyst is modified to the extent that it becomes

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highly regioselective for the para-isomer, in which case insufficient quantities of the meta isomer are produced.

In the present process, however, the activity and selectivity of the catalyst are modified together and used in combination with selected reaction parameter to produce an ethyltoluene product with the required isomer distribution. In addition to giving the desired high meta content material with a very low ortho content, the proportion of ethylbenzene by-product, produced by disproportionation of the toluene feed, is minimized by controlling the activity of the catalyst to inhibit the disproportionation reaction while maintaining a sufficient contact time (reciprocal space velocity) to shift the composition of the desired ethyltoluene product to the desired isomer distribution.

The catalyst includes aluminosilicate zeolite ZSM-5 as the essential catalytic component. This zeolite, an intermediate pore size zeolite, is matrixed with a binder such as alumina in order to give sufficient strength to the catalyst and in order to avoid binder effects a low acidity material is preferred. The ZSM-5 should have a crystallite size of at least one micron in order to provide the desired diffusion characteristics and crystallite sizes of about 1.5 microns or more e.g. 2 micron are preferred. ZSM-5 with this crystal size may be readily made by conventional techniques using substituted ammonium directing agents such as tetrapropylammonium cations in combination with trimethylammonium cations, as described in U.S. 4,375,458 (Dwyer) to which reference is made for a description of such a technique.

Activity of the zeolite is maintained at a controlled, relatively low level, by steaming the original zeolite in order to reduce the incidence of side reactions such as the toluene disproportionation reaction. The acid activity of the catalyst should be maintained at an alpha value of not more than 80 and not

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greater than 50. It has been found that an alpha value of about 30 gives good results.

5 The alpha value is an approximate indication of the catalytic cracking activity of the catalyst compared to a standard catalyst. The alpha test gives the relative
10 rate constant (rate of normal hexane conversion per volume of catalyst per unit time) of the test catalyst relative to the standard catalyst which is taken as an alpha of 1 (Rate Constant = 0.016 sec^{-1}). The alpha test is described in U.S. Patent 3,354,078 and in J. Catalysis, 4, 527 (1965); 6, 278 (1966); and 61, 395 (1980), to which reference is made for a description of the test. The experimental conditions of the test used
15 to determine the alpha values referred to in this specification include a constant temperature of 538°C and a variable flow rate as described in detail in J. Catalysis, 61, 395 (1980).

20 Production of the desired acidic activity level by steaming has been found to be an essential feature of the process: the use of low activity, highly siliceous zeolites does not result in the production of the desired high meta content ethyltoluene product. Normally, a silica:alumina ratio of about 70:1 in the zeolite prior to steaming to the final alpha value will
25 give good results for the finished catalyst.

The reaction is carried out by passing toluene and ethylene together over the ZSM-5 catalyst at temperatures in the range of about 500° to about 850°F (about 260° to 455°C). The contact time (reciprocal
30 space velocity) is maintained at a value which enables the product composition to shift sufficiently to give the desired content of the meta isomer while maintaining the ortho content at the necessary low level. Because reaction temperature and contact time are both related
35 to total reaction severity, a trade off may be affected between temperature and space velocity with decreasing space velocity increasing the content of the meta and

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ortho isomers. Normally, temperatures will be from about 750° to 850°F (about 400° to 455°C) with space velocities, based on the toluene feed, from 10 to 40 WHSV.

5 The relatively high velocities are important. In a commercial process, higher space velocities enable more product to be produced in a unit of a given size. Additionally, we discovered that the space velocity contributes to a product mixture that contains
10 high amounts of the meta-isomer and only minimal amounts of the ortho-isomer.

 The reaction is not critical with respect to pressure and for reasons of economy it will be convenient to operate at low to moderate pressures,
15 typically up to about 500 psig (about 3550 kPa abs.) although higher pressures may be used if desired. A relatively high ratio of toluene to ethylene is preferred in order to ensure a high selectivity of ethylene to ethyltoluene. Typically, the ratio of
20 toluene to ethylene will be from 2:1 to about 30:1 and in most cases ratios from 10:1 to 20:1 (molar) will be satisfactory.

Example 1

 Three different ZSM-5/alumina catalysts were tested
25 in the ethylation of toluene. The catalyst were as follows:

Catalyst A: unsteamed ZSM-5, crystallite size >1
 micron, 358 alpha
Catalyst B: steamed ZSM-5, crystallite size >1
30 micron, 70 alpha
Catalyst C: steamed ZSM-5, crystallite size >1
 micron, 30 alpha.

 Toluene and ethylene were passed over the catalysts at temperatures from 810° to 835°F (432° to 446°C) at a
35 pressure of 150 psig (1130 kPa abs). The space velocity based on the toluene feed was 130 WHSV. A

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toluene: ethylene mole ratio of 16 was employed. The results are given in Table 1 below.

Table 1
Ethyltoluene Production over ZSM-5

5	<u>Catalyst</u>	<u>A</u> 358 α	<u>B</u> 70 α	<u>C</u> 30 α
	Temperature, °F	814	817	832
	Pressure, psig	150	150	150
	WHSV (Toluene)	130	130	130
10	Toluene/C2=(mol)	16	16	16
	<u>Normalized Ethyltoluene %</u>			
	para	51.8	60.9	69.7
	meta	46.7	38.7	30.0
	ortho	1.5	0.4	0.3
15	<u>Liquid Products, wt%</u>			
	Light Gas	0.35	1.85	0.16
	Benzene	4.49	0.67	0.97
	EB	1.98	0.84	0.81
	Xylenes	6.82	3.37	2.58
20	p-ET	42.88	56.40	66.52
	m-ET	38.65	35.86	28.62
	o-ET	1.21	0.34	0.32
	C10+ Aromatics	3.62	0.67	- -
25	Total ET	82.74	92.60	95.46
	Bz + EB + Xy	13.29	4.88	4.36
	Other	3.97	2.52	0.18
	[Bz+EB]/Xyl, mol	1.20	0.53	0.82

* Reactor inlet

Example 2

30 The effect of reaction severity (contact time, temperature) was investigated using the steamed ZSM-5 30 alpha catalyst (Catalyst C) above. Toluene ethylation was carried out at temperatures from 760° to about 790°F (404 to 421 °C) (reactor inlet). Space velocity based on

35 the toluene feed varied from 20 to 130 (WHSV). A toluene:ethylene mole ratio of 7 or 16 was used at a pressure of 150 psig. No hydrogen was added. The results are shown in Table 2 below.

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Table 2
Ethyltoluene Production - Reaction Severity

5	TOS, hr	26	2	6	9
	Temp. °F	781	788	787	762
	WHSV (toluene)	20	40	60	130
	Tol/C ₂ =(mole)	7	7	7	16
	P, psig	150	150	150	150
<u>Normalized Ethyltoluene. %</u>					
10	p-ET	33.39	55.04	66.31	77.43
	m-ET	65.60	44.61	33.42	22.39
	o-ET	1.01	0.35	0.27	0.18
<u>Liquid Products, wt%</u>					
15	Light gas	0.30	0.14	-	0.17
	Benzene	1.98	0.56	0.41	0.50
	EB	1.14	0.79	0.67	0.83
	xyl	3.27	1.45	1.44	2.00
	p-ET	29.96	52.29	64.51	74.72
	m-ET	58.87	42.39	32.51	21.61
20	o-ET	0.91	0.33	0.26	0.17
	C ₁₀ + Aromatics	3.57	2.05	0.21	-
	Total ET	89.74	95.01	97.33	96.50
	Bz+EB+Xyl	6.39	2.80	2.52	3.33
	Other	3.87	2.19	0.15	0.17
	[Bz+EB]/Xyl, mol	1.17	1.08	0.93	0.75

25 *Reactor Inlet.

The results in Table 3 show that production of the meta isomer increases with increasing contact time (lower numerical space velocity) but is accompanied by an increase in the level of the undesired ortho isomer.

30 By selection of reaction severity the ortho isomer may be maintained below 0.5% while obtaining a high level of the meta isomer.

Example 3

35 Toluene was ethylated over the steamed, 30 alpha ZSM-5 catalyst with hydrogen co-feed at total system pressures (reactor inlet) up to 250 psig blank kpa abs) the results are shown in Table 3 below.

40 The results show that the hydrogen co-feed does not affect the distribution of the ethyltoluene isomers significantly (compare Table 2 above), but slightly decreases the disproportionation activity. In these

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studies, however, relatively long contact times were used and the content of the undesired ortho ethyltoluene isomer may exceed acceptable levels when operating at greater severity.

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Table 3
Ethyltoluene Production - H₂ Co-Feed

	TOS, hr	26	7	10
	Temp. °F	781	816	810
	WHSV (toluene)	20	20	20
10	Tol/C ₂ =/H ₂ (mole)	7/1	7/1	7/1/5
	P, psig	150	150	250
	<u>Normalized Ethyltoluene, %</u>			
	p-ET	33.39	31.63	34.53
	m-ET	65.60	67.01	64.47
15	o-ET	1.01	1.36	1.00
	<u>Liquid Products, wt%</u>			
	Light gas	0.30	0.66	0.08
	Benzene	1.98	3.37	1.96
	EB	1.14	1.54	1.13
20	xyl	3.27	4.68	3.84
	p-ET	29.96	27.23	31.23
	m-ET	58.87	57.69	58.31
	o-ET	0.91	1.17	0.90
	C ₁₀ + Aromatics	3.57	3.66	2.63
25	Total ET	89.74	86.09	90.44
	Bz+EB+Xyl	6.39	9.59	6.93
	Other	3.87	4.32	2.63
	[Bz+EB]/Xyl, mol	1.17	1.31	0.99

* Reactor inlet

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Example 4

Three runs were made using a low alpha (alpha = 16) highly siliceous ZSM-5 with a crystal size of 2 microns. The reaction was carried out at higher temperatures in order to compensate for the lower acidity of the catalyst, with the temperature varying from 820° to 850°F (438 to 455°C) at the reactor inlet. The reaction was carried out in the absence of hydrogen at a toluene:ethylene molar ratio of 16:1. Space velocities varied inversely with temperature from 60 to 130. The results are shown in Table 4 below.

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Table 4
Ethyltoluene Production - High Silica ZSM-5

	TOS, hr	3	6	9
	Temp. °F*	823	845	850
5	WHSV(toluene)	130	80	60
	Tol/C ₂ = (mole)	16	16	16
	<u>Normalized Ethyltoluene, %</u>			
	p-ET	79.57	72.86	67.36
	m-ET	20.05	26.80	32.01
10	o-ET	0.38	0.34	0.63
	<u>Liquid Products, wt%</u>			
	Light gas	0.70	0.60	0.72
	Benzene	1.29	2.18	3.64
	EB	1.05	1.41	1.64
15	Xyl	3.85	5.01	6.38
	p-ET	74.10	66.16	59.02
	m-ET	18.67	24.34	28.05
	o-ET	0.35	0.31	0.55
	C ₁₀ + Aromatics		Total	73.90.81.07
20	Bz+EB+Xyl	6.19	8.60	11.66
	Other	0.69	0.59	0.72
	[Bz+EB]/Xyl, mol	0.72	1.00	1.05

* Reactor inlet

The results in Table 4 above show that a low content of the ortho isomer may be obtained in the product using the highly siliceous zeolite but that this is not accompanied by an adequately high level for the meta isomer.

Example 5

The effect of the ZSM-5 crystal size was investigated with two ZSM-5 catalysts. The first catalyst (Catalyst D) had an alpha value of 50 and a zeolite crystal size of less than 0.05 μ and the second (Catalyst E) an alpha value of 18 and a crystal size between 0.1 and 1 μ . The two catalysts were used to ethylate toluene at temperatures from about 780° to 860°F (about 415 to 460°C) in the absence of hydrogen at a pressure of 150 psig (1135 kPaa). The results for Catalyst D are given in Table 5 and for Catalyst E in Table 6 below.

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Table 5
Ethyltoluene Synthesis - 50 alpha ZSM-5

5	TOS, hr	8
	Temp, °F	816
	WHSV (toluene)	130
	Tol/C ₂ =	7/1
	P, psig	150
<u>Normalized Ethyltoluene, %</u>		
10	p-ET	31.31
	m-ET	63.26
	o-ET	5.44
<u>Liquid Products, wt%</u>		
15	Light gas	0.46
	Benzene	2.19
	EB	4.47
	Xyl	6.58
	p-ET	27.03
	m-ET	54.58
	o-ET	4.70
20	Total ET	86.31
	Bz+EB+Xyl	13.24
	Other	0.45
	[Bz+EB]/Xyl, mole	1.13

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Table 6
Ethyltoluene Synthesis - 18 alpha ZSM-5

5	TOS, hr	2	12
	Temp. °F	812	787
	WHSV (Toluene)	20	20
	Tol/C ₂ =/H ₂	7/1	7/1
	P, psig	150	150
<u>Normalized Ethyltoluene, %</u>			
10	p-ET	28.61	30.05
	m-ET	63.62	66.21
	o-ET	7.87	3.73
<u>Liquid Products, wt%</u>			
15	Light gas	0.14	0.08
	Benzene	1.79	1.31
	EB	1.00	0.77
	Xyl	2.76	2.00
	p-ET	26.36	28.38
20	m-ET	58.52	62.46
	o-ET	7.25	3.54
	C ₁₀ + Aromatics	2.28	1.46
	Total ET	92.13	94.38
	Bz+EB+Xyl	5.55	4.08
25	Other	2.32	1.54
	[Bz+EB]/Xyl, mol	1.24	1.27

* Reactor inlet

The results given above show that the crystal size of the zeolite component of the catalyst affected the isomer distribution of the ethyltoluene product: the catalysts with the low acidity, smaller crystal ZSM-5 do not achieve the low ortho-isomer content which is attainable with the low acidity, larger crystal catalysts of Example 1 above (Catalysts B, C), under comparable conditions.

Example 6

The effect of increasing space velocity on the proportion of meta-isomer in the product was investigated using a steamed ZSM-5 catalyst having an alpha value of about 30.

The four cases reported in Table 7 show the results obtained at four different times on stream (OS) in a two-bed operation at temperatures within the range of



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775°-800°F. The space velocity of the reactants, reported as WHSV toluene, was varied from about 15 to about 42 to obtain the results shown.

Table 7
Mobil Ethyltoluene (MET) Catalyst - Two-Bed Operation

Case	A	B	C	D
Hours OS	8	44	46	68
T(avg), °F				
Bed #1	775	778	797	800
Bed #2	760	763	783	796
Tol WHSV	41.8	21.2	21.8	15.2
Tol/C ₂ =/H ₂ , mol	8/1/7	5/1/7	6/1/8	7/1/18
Press, psig	250	252	252	200
ET Isomers, %				
m	43.4	51.1	54.1	57.9
p	56.2	48.3	45.1	41.0
o	0.5	0.6	0.8	1.1
Total ET, wt%	14.1	22.3	18.1	19.5
Byproduct, wt%				
Bz+EB+Xy	0.89	1.05	1.00	1.15
Hvy	0.17	0.44	0.24	0.23
ET Prod, lb/hr	9,500	7,800	6,000	4,000

The results show that as the space velocity increases, the proportion of the meta-isomer in the product, decreases. At the same time, the proportion of the ortho-isomer decreases. The effect of increasing space velocity is therefore to move the composition of the isomer mixture away from equilibrium values, while a decreased velocity will produce a trend towards equilibrium. The content of the ortho-isomer in the product tends to increase along with the meta at progressively lower space velocities.

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CLAIMS

1. A process for the production of an ethyltoluene isomer mixture of high m-isomer and very low o-isomer content, which comprises ethylating toluene with
5 ethylene in the presence of a catalyst comprising ZSM-5 having a crystallite size of at least one micron and which has been steamed to an alpha value not more than 80, at a temperature from 700° to 900°F and a space velocity, based on the toluene feed, from 10 to 150
10 WHSV, to produce a reaction product comprising a mixture of isomers of ethyltoluene in which the weight ratio of the m-isomer to the p-isomer is at least 1:1, and of the o-isomer is not more than 1.5 wt%.
2. A process according to claim 1 in which the weight
15 ratio of the m-isomer to the p-isomer in the ethyltoluene isomer mixture is at least 1.2:1.
3. A process according to claim 1 in which the content of the o-isomer in the ethyltoluene isomer mixture is not more than 1 wt%.
- 20 4. A process according to claim 1 in which the content of the o-isomer in the ethyltoluene isomer mixture is not more than 0.5 wt%.
5. A process according to claim 1 in which the crystallite size of the ZSM-5 is at least 2 microns.
- 25 6. A process according to claim 1 in which the catalyst has an alpha value not greater than 50.
7. A process according to claim 5 in which the catalyst has an alpha value not greater than 40.
8. A process according to claim 1 in which the toluene
30 is reacted with the ethylene at a temperature from 750° to 850°C.

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PRODUCTION OF ETHYLTOLUENE

Abstract

Ethyltoluene is produced by ethylating toluene in the presence of a ZSM-5 catalyst of controlled acidity and diffusivity to produce an ethyltoluene isomer mixture which is high in the content of the meta isomer and very low in the ortho isomer. The weight ratio of the meta isomer to the para-isomer is at least 1:1, preferably at least 1.2:1 while the ortho isomer is kept below 1.5%, preferably below 0.5%. The product ethyltoluene may be dehydrogenated to form polymerization grade vinyl toluene.

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PRODUCTION OF ETHYLTOLUENE

This invention relates to a process for the production of ethyltoluene and more particularly, to a process for the production of a mixture of ethyltoluene isomers having a high content of the meta isomer and a very low quantity of the ortho isomer.

Vinyl toluene is an important industrial commodity chemical used for the production of polymers. For certain purposes, it is desirable to produce vinyl toluene with a relatively high content of the meta isomer (m-methyl styrene), typically from 50 to 70% of the total vinyl toluene content. At the same time, a very low content of the ortho isomer (o-methyl styrene) is desired since this material acts as a chain stopper in polymerization. Normally, a maximum content of the ortho isomer of 1.5% and preferably below 1 or 0.5% must be adhered to for a commercially acceptable material.

Vinyl toluene is produced from ethyltoluene by dehydrogenation with the isomer ratio of the vinyl toluene product being directly dependent upon the isomer ratio of the ethyltoluene precursor. Thus, the ethyltoluene should typically contain from 50 to 70% of the meta isomer and not more than 1% ortho isomer with the balance being made up of the para isomer.

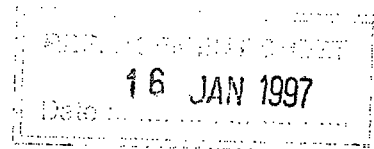
Ethyltoluene may be produced by the ethylation of toluene in the presence of an acidic catalyst and for this purpose, Lewis acid type catalysts such as aluminum chloride as well as heterogeneous zeolite catalyst have been used. Homogenous phase Lewis acid catalysts such as aluminum trichloride are effective for the ethylation of toluene under relatively mild conditions to produce an ethyltoluene product in which the isomer ratio is relatively close to the equilibrium ratio of 31.5% para, 50.2% meta and 18.3% ortho. U. S. Patent No. 4,143,084 (Kaeding), for example, discloses (Example 13) a process

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in which toluene is ethylated in the presence of aluminum chloride to produce ethyltoluene with a p-m-o- isomer ratio of 27:60:13. While this ethyltoluene product has the requisite content of the meta isomer, the ortho isomer is present in excessive amounts.

An intermediate pore size zeolite such as ZSM-5 may be used to catalyze the ethylation of toluene, typically using temperatures in the range of 500° to 850°F (260° to 455°C). The isomer ratio of the product varies according to the specific shape selectivity characteristics of the zeolite component of the catalyst. If ZSM-5 is used in its hydrogen form without modification, the ethyltoluene product has an isomer ratio which is relatively close to equilibrium. An example of this is given in U. S. 4,086,287 where Example 3 shows that a meta content of about 60% may be obtained but that the ortho isomer is present in excessive amounts.

It is possible to modify zeolite catalysts so that selectivity for the para isomer is increased significantly above the equilibrium level. For example, by increasing the crystallite size of ZSM-5 the ratio of para to meta isomer may be raised significantly with a corresponding loss in the amount of the ortho isomer. U. S. 4,086,287 (Example 4) shows that ortho contents as low as about 1.6% may be obtained with meta contents of about 65% using a large crystal ZSM-5 catalyst. Even here however, the content of the ortho isomer is excessive. High temperatures and relatively low space velocities result in more of the meta-isomer and less of the ortho U.S. 4,086,287 (Example 4). However, higher space velocities in a commercial process are desirable because they enable more product to be produced in a unit of given size and from Example 4 there is no indication that higher space velocities will achieve the preferred isomer ratio.



By suitable modification of the diffusion characteristics of the zeolite, the content of the ortho isomer may be reduced to suitably low levels but this is accompanied by a major increase in the selectivity to the para isomer to the extent that the process is highly regioselective. When ZSM-5 is modified with magnesium, phosphorous or boron, the content of the ortho isomer may be reduced almost to zero but in this case, selectivity for the para isomer is exceptionally high so that the ethyltoluene product does not have the desired balance of the para and meta isomer components. Processes such as this are described in U. S. Patents No. 4,086,287 and 4,143,084.

U.S. Patent No. 4,489,214 (Butler) discloses a process for producing ethyltoluene using a catalytic material described as "silicalite", a material known to be a highly siliceous form of zeolite ZSM-5. See Fyfe et al., "Resolving crystallographically distinct sites in silicalite and ZSM-5 by solid state NMR", *Nature* 296, 530 (1982) and Olson, D. H. et al., *J. Catalysis* 61, 390-396 (1980).

In summary, therefore, the problem remains of producing ethyltoluene with a relatively high content of the meta isomer and a low content of the ortho isomer not exceeding 1.5% and preferably less than 0.5%.

We have now devised a process for the production of ethyltoluene which has a relatively high content of the meta isomer and a low content of the ortho isomer. The m:-p- ratio of the product is at least 1:1 (m:-p-) and preferably at least 1.5:1 by weight; the level of the ortho isomer does not, in any event, exceed 1.5% and is usually below 1%. This result is achieved by suitable selection of catalyst and process constraints in the reaction.

The ethyltoluene product is produced by the ethylation of toluene in the presence of an intermediate pore size aluminosilicate zeolite catalyst of controlled

acidity produced by steaming. The reaction is typically carried out at temperatures from 700° to 900 °F (about 370° to 480°C) with toluene:ethylene ratios from about 2:1 to 20:1 and space velocities based on the toluene feed, of about 10 to 40 (WHSV). The temperature will normally not exceed about 850°F (about 455°C).

In the present process toluene is reacted with ethylene in the presence of an intermediate pore size steamed aluminosilicate zeolite catalyst. The objective is to produce an ethyltoluene product which has a high content of the meta isomer and a very low content of the ortho isomer. The meta: para ratio of the product is at least 1:1 by weight (equivalent to at least 50 weight percent of the meta-isomer on an ortho-free basis) and is preferably at least 1.2:1 (at least 55 weight percent meta- on an ortho-free basis). In all cases, however, the maximum content of the ortho isomer is to be maintained at 1.5% and should preferably be below 1% or, better, 0.5% by weight if the ethyltoluene product is to be used for a polymerization grade vinyltoluene.

When toluene is reacted with ethylene in the presence of the shape selective heterogeneous catalyst such as ZSM-5, the initial product is probably the para-ethyltoluene which is progressively converted to the meta- and then to the ortho- isomers as contact with the acidic catalyst continues. As reaction severity increases, movement towards equilibrium is accelerated correspondingly and it therefore becomes difficult to produce a product containing relatively large amount of the meta isomer while, at the same time maintaining the content of the ortho isomer at very low levels. Normally, as shown by the Kaeding patents mentioned above, production of the meta isomer is accompanied by increasing amount of the ortho isomer as the composition of the reaction product moves toward equilibrium in the presence of the catalyst unless the shape selectivity of the catalyst is modified to the extent that it becomes

highly regioselective for the para-isomer, in which case insufficient quantities of the meta isomer are produced.

In the present process, however, the activity and selectivity of the catalyst are modified together and used in combination with selected reaction parameter to produce an ethyltoluene product with the required isomer distribution. In addition to giving the desired high meta content material with a very low ortho content, the proportion of ethylbenzene by-product, produced by disproportionation of the toluene feed, is minimized by controlling the activity of the catalyst to inhibit the disproportionation reaction while maintaining a sufficient contact time (reciprocal space velocity) to shift the composition of the desired ethyltoluene product to the desired isomer distribution.

The catalyst includes aluminosilicate zeolite ZSM-5 as the essential catalytic component. This zeolite, an intermediate pore size zeolite, is matrixed with a binder such as alumina in order to give sufficient strength to the catalyst and in order to avoid binder effects a low acidity material is preferred. The ZSM-5 should have a crystallite size of at least one micron in order to provide the desired diffusion characteristics and crystallite sizes of about 1.5 microns or more e.g. 2 micron are preferred. ZSM-5 with this crystal size may be readily made by conventional techniques using substituted ammonium directing agents such as tetrapropylammonium cations in combination with trimethylammonium cations, as described in U.S. 4,375,458 (Dwyer) to which reference is made for a description of such a technique.

Activity of the zeolite is maintained at a controlled, relatively low level, by steaming the original zeolite in order to reduce the incidence of side reactions such as the toluene disproportionation reaction. The acid activity of the catalyst should be maintained at an alpha value of not more than 80 and not

greater than 50. It has been found that an alpha value of about 30 gives good results.

The alpha value is an approximate indication of the catalytic cracking activity of the catalyst compared to a standard catalyst. The alpha test gives the relative rate constant (rate of normal hexane conversion per volume of catalyst per unit time) of the test catalyst relative to the standard catalyst which is taken as an alpha of 1 (Rate Constant = 0.016 sec^{-1}). The alpha test is described in U.S. Patent 3,354,078 and in J. Catalysis, 4, 527 (1965); 6, 278 (1966); and 61, 395 (1980), to which reference is made for a description of the test. The experimental conditions of the test used to determine the alpha values referred to in this specification include a constant temperature of 538°C and a variable flow rate as described in detail in J. Catalysis, 61, 395 (1980).

Production of the desired acidic activity level by steaming has been found to be an essential feature of the process: the use of low activity, highly siliceous zeolites does not result in the production of the desired high meta content ethyltoluene product. Normally, a silica:alumina ratio of about 70:1 in the zeolite prior to steaming to the final alpha value will give good results for the finished catalyst.

The reaction is carried out by passing toluene and ethylene together over the ZSM-5 catalyst at temperatures in the range of about 500° to about 850°F (about 260° to 455°C). The contact time (reciprocal space velocity) is maintained at a value which enables the product composition to shift sufficiently to give the desired content of the meta isomer while maintaining the ortho content at the necessary low level. Because reaction temperature and contact time are both related to total reaction severity, a trade off may be affected between temperature and space velocity with decreasing space velocity increasing the content of the meta and

ortho isomers. Normally, temperatures will be from about 750° to 850°F (about 400° to 455°C) with space velocities, based on the toluene feed, from 10 to 40 WHSV.

The relatively high velocities are important. In a commercial process, higher space velocities enable more product to be produced in a unit of a given size. Additionally, we discovered that the space velocity contributes to a product mixture that contains high amounts of the meta-isomer and only minimal amounts of the ortho-isomer.

The reaction is not critical with respect to pressure and for reasons of economy it will be convenient to operate at low to moderate pressures, typically up to about 500 psig (about 3550 kPa abs.) although higher pressures may be used if desired. A relatively high ratio of toluene to ethylene is preferred in order to ensure a high selectivity of ethylene to ethyltoluene. Typically, the ratio of toluene to ethylene will be from 2:1 to about 30:1 and in most cases ratios from 10:1 to 20:1 (molar) will be satisfactory.

Example 1

Three different ZSM-5/alumina catalysts were tested in the ethylation of toluene. The catalyst were as follows:

- Catalyst A: unsteamed ZSM-5, crystallite size >1 micron, 358 alpha
Catalyst B: steamed ZSM-5, crystallite size >1 micron, 70 alpha
Catalyst C: steamed ZSM-5, crystallite size >1 micron, 30 alpha.

Toluene and ethylene were passed over the catalysts at temperatures from 810° to 835°F (432° to 446°C) at a pressure of 150 psig (1130 kPa abs). The space velocity based on the toluene feed was 130 WHSV. A

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toluene: ethylene mole ratio of 16 was employed. The results are given in Table 1 below.

Table 1
Ethyltoluene Production over ZSM-5

<u>Catalyst</u>	<u>A</u> 358 α	<u>B</u> 70 α	<u>C</u> 30 α
Temperature, °F	814	817	832
Pressure, psig	150	150	150
WHSV (Toluene)	130	130	130
Toluene/C2=(mol)	16	16	16
<u>Normalized Ethyltoluene %</u>			
para	51.8	60.9	69.7
meta	46.7	38.7	30.0
ortho	1.5	0.4	0.3
<u>Liquid Products, wt%</u>			
Light Gas	0.35	1.85	0.16
Benzene	4.49	0.67	0.97
EB	1.98	0.84	0.81
Xylenes	6.82	3.37	2.58
p-ET	42.88	56.40	66.52
m-ET	38.65	35.86	28.62
o-ET	1.21	0.34	0.32
C10+ Aromatics	3.62	0.67	- -
Total ET	82.74	92.60	95.46
Bz + EB + Xy	13.29	4.88	4.36
Other	3.97	2.52	0.18
[Bz+EB]/Xyl, mol	1.20	0.53	0.82

* Reactor inlet

Example 2

The effect of reaction severity (contact time, temperature) was investigated using the steamed ZSM-5 30 alpha catalyst (Catalyst C) above. Toluene ethylation was carried out at temperatures from 760° to about 790°F (404 to 421 °C) (reactor inlet). Space velocity based on the toluene feed varied from 20 to 130 (WHSV). A toluene:ethylene mole ratio of 7 or 16 was used at a pressure of 150 psig. No hydrogen was added. The results are shown in Table 2 below.

Table 2
Ethyltoluene Production - Reaction Severity

TOS, hr	26	2	6	9
Temp. °F	781	788	787	762
WHSV (toluene)	20	40	60	130
Tol/C ₂ =(mole)	7	7	7	16
P, psig	150	150	150	150
Normalized Ethyltoluene.%				
p-ET	33.39	55.04	66.31	77.43
m-ET	65.60	44.61	33.42	22.39
o-ET	1.01	0.35	0.27	0.18
Liquid Products, wt%				
Light gas	0.30	0.14	-	0.17
Benzene	1.98	0.56	0.41	0.50
EB	1.14	0.79	0.67	0.83
xyl	3.27	1.45	1.44	2.00
p-ET	29.96	52.29	64.51	74.72
m-ET	58.87	42.39	32.51	21.61
o-ET	0.91	0.33	0.26	0.17
C ₁₀ + Aromatics	3.57	2.05	0.21	-
Total ET	89.74	95.01	97.33	96.50
Bz+EB+Xyl	6.39	2.80	2.52	3.33
Other	3.87	2.19	0.15	0.17
[Bz+EB]/Xyl, mol	1.17	1.08	0.93	0.75

*Reactor Inlet.

The results in Table 3 show that production of the meta isomer increases with increasing contact time (lower numerical space velocity) but is accompanied by an increase in the level of the undesired ortho isomer. By selection of reaction severity the ortho isomer may be maintained below 0.5% while obtaining a high level of the meta isomer.

Example 3

Toluene was ethylated over the steamed, 30 alpha ZSM-5 catalyst with hydrogen co-feed at total system pressures (reactor inlet) up to 250 psig blank kpa abs) the results are shown in Table 3 below.

The results show that the hydrogen co-feed does not affect the distribution of the ethyltoluene isomers significantly (compare Table 2 above), but slightly decreases the disproportionation activity. In these

studies, however, relatively long contact times were used and the content of the undesired ortho ethyltoluene isomer may exceed acceptable levels when operating at greater severity.

Table 3
Ethyltoluene Production - H₂ Co-Feed

TOS, hr	26	7	10
Temp. °F	781	816	810
WHSV (toluene)	20	20	20
Tol/C ₂ =/H ₂ (mole)	7/1	7/1	7/1/5
P, psig	150	150	250
<u>Normalized Ethyltoluene, %</u>			
p-ET	33.39	31.63	34.53
m-ET	65.60	67.01	64.47
o-ET	1.01	1.36	1.00
<u>Liquid Products, wt%</u>			
Light gas	0.30	0.66	0.08
Benzene	1.98	3.37	1.96
EB	1.14	1.54	1.13
xyl	3.27	4.68	3.84
p-ET	29.96	27.23	31.23
m-ET	58.87	57.69	58.31
o-ET	0.91	1.17	0.90
C ₁₀ + Aromatics	3.57	3.66	2.63
Total ET	89.74	86.09	90.44
Bz+EB+Xyl	6.39	9.59	6.93
Other	3.87	4.32	2.63
[Bz+EB]/Xyl, mol	1.17	1.31	0.99

* Reactor inlet

Example 4

Three runs were made using a low alpha (alpha = 16) highly siliceous ZSM-5 with a crystal size of 2 microns. The reaction was carried out at higher temperatures in order to compensate for the lower acidity of the catalyst, with the temperature varying from 820° to 850°F (438 to 455°C) at the reactor inlet. The reaction was carried out in the absence of hydrogen at a toluene:ethylene molar ratio of 16:1. Space velocities varied inversely with temperature from 60 to 130. The results are shown in Table 4 below.

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Table 4
Ethyltoluene Production - High Silica ZSM-5

TOS, hr	3	6	9
Temp. °F*	823	845	850
WHSV(toluene)	130	80	60
Tol/C ₂ = (mole)	16	16	16
<u>Normalized Ethyltoluene, %</u>			
p-ET	79.57	72.86	67.36
m-ET	20.05	26.80	32.01
o-ET	0.38	0.34	0.63
<u>Liquid Products, wt%</u>			
Light gas	0.70	0.60	0.72
Benzene	1.29	2.18	3.64
EB	1.05	1.41	1.64
Xyl	3.85	5.01	6.38
p-ET	74.10	66.16	59.02
m-ET	18.67	24.34	28.05
o-ET	0.35	0.31	0.55
C ₁₀ + Aromatics		Total	93.92
Bz+EB+Xyl	6.19	8.60	11.66
Other	0.69	0.59	0.72
[Bz+EB]/Xyl, mol	0.72	1.00	1.05

* Reactor inlet

The results in Table 4 above show that a low content of the ortho isomer may be obtained in the product using the highly siliceous zeolite but that this is not accompanied by an adequately high level for the meta isomer.

Example 5

The effect of the ZSM-5 crystal size was investigated with two ZSM-5 catalysts. The first catalyst (Catalyst D) had an alpha value of 50 and a zeolite crystal size of less than 0.05 μ and the second (Catalyst E) an alpha value of 18 and a crystal size between 0.1 and 1 μ . The two catalysts were used to ethylate toluene at temperatures from about 780° to 860°F (about 415 to 460°C) in the absence of hydrogen at a pressure of 150 psig (1135 kPaa). The results for Catalyst D are given in Table 5 and for Catalyst E in Table 6 below.

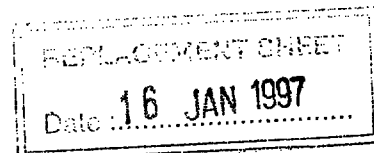


Table 5
Ethyltoluene Synthesis - 50 alpha ZSM-5

TOS, hr	8
Temp, °F	816
WHSV (toluene)	130
Tol/C ₂ =	7/1
P, psig	150

Normalized Ethyltoluene, %

p-ET	31.31
m-ET	63.26
o-ET	5.44

Liquid Products, wt%

Light gas	0.46
Benzene	2.19
EB	4.47
Xyl	6.58
p-ET	27.03
m-ET	54.58
o-ET	4.70

Total ET	86.31
Bz+EB+Xyl	13.24
Other	0.45
[Bz+EB]/Xyl, mole	1.13

Table 6
Ethyltoluene Synthesis - 18 alpha ZSM-5

TOS, hr	2	12
Temp. °F	812	787
WHSV (Toluene)	20	20
Tol/C ₂ =/H ₂	7/1	7/1
P, psig	150	150
<u>Normalized Ethyltoluene, %</u>		
p-ET	28.61	30.05
m-ET	63.62	66.21
o-ET	7.87	3.73
<u>Liquid Products, wt%</u>		
Light gas	0.14	0.08
Benzene	1.79	1.31
EB	1.00	0.77
Xyl	2.76	2.00
p-ET	26.36	28.38
m-ET	58.52	62.46
o-ET	7.25	3.54
C ₁₀ + Aromatics	2.28	1.46
Total ET	92.13	94.38
Bz+EB+Xyl	5.55	4.08
Other	2.32	1.54
[Bz+EB]/Xyl, mol	1.24	1.27

* Reactor inlet

The results given above show that the crystal size of the zeolite component of the catalyst affected the isomer distribution of the ethyltoluene product: the catalysts with the low acidity, smaller crystal ZSM-5 do not achieve the low ortho-isomer content which is attainable with the low acidity, larger crystal catalysts of Example 1 above (Catalysts B, C), under comparable conditions.

Example 6

The effect of increasing space velocity on the proportion of meta-isomer in the product was investigated using a steamed ZSM-5 catalyst having an alpha value of about 30.

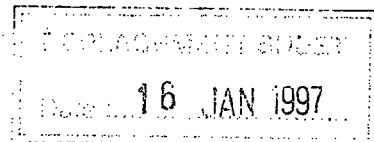
The four cases reported in Table 7 show the results obtained at four different times on stream (OS) in a two-bed operation at temperatures within the range of

775°-800°F. The space velocity of the reactants, reported as WHSV toluene, was varied from about 15 to about 42 to obtain the results shown.

Table 7
Mobil Ethyltoluene (MET) Catalyst - Two-Bed Operation

<u>Case</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
Hours OS	8	44	46	68
T(avg), °F				
Bed #1	775	778	797	800
Bed #2	760	763	783	796
Tol WHSV	41.8	21.2	21.8	15.2
Tol/C ₂ =/H ₂ , mol	8/1/7	5/1/7	6/1/8	7/1/18
Press, psig	250	252	252	200
ET Isomers, %				
m	43.4	51.1	54.1	57.9
p	56.2	48.3	45.1	41.0
o	0.5	0.6	0.8	1.1
Total ET, wt%	14.1	22.3	18.1	19.5
Byproduct, wt%				
Bz+EB+Xy	0.89	1.05	1.00	1.15
Hvy	0.17	0.44	0.24	0.23
ET Prod, lb/hr	9,500	7,800	6,000	4,000

The results show that as the space velocity increases, the proportion of the meta-isomer in the product, decreases. At the same time, the proportion of the ortho-isomer decreases. The effect of increasing space velocity is therefore to move the composition of the isomer mixture away from equilibrium values, while a decreased velocity will produce a trend towards equilibrium. The content of the ortho-isomer in the product tends to increase along with the meta at progressively lower space velocities.



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CLAIMS

1. A process for the production of an ethyltoluene isomer mixture of high m-isomer and very low o-isomer content, which comprises ethylating toluene with ethylene in the presence of a catalyst comprising ZSM-5 having a crystallite size of at least one micron and which has been steamed to an alpha value not more than 80, at a temperature from 700° to 900°F and a space velocity, based on the toluene feed, from 10 to 150 WHSV, to produce a reaction product comprising a mixture of isomers of ethyltoluene in which the weight ratio of the m-isomer to the p-isomer is at least 1:1, and of the o-isomer is not more than 1.5 wt%.
2. A process according to claim 1 in which the weight ratio of the m-isomer to the p-isomer in the ethyltoluene isomer mixture is at least 1.2:1.
3. A process according to claim 1 in which the content of the o-isomer in the ethyltoluene isomer mixture is not more than 1 wt%.
4. A process according to claim 1 in which the content of the o-isomer in the ethyltoluene isomer mixture is not more than 0.5 wt%.
5. A process according to claim 1 in which the crystallite size of the ZSM-5 is at least 2 microns.
6. A process according to claim 1 in which the catalyst has an alpha value not greater than 50.
7. A process according to claim 5 in which the catalyst has an alpha value not greater than 40.
8. A process according to claim 1 in which the toluene is reacted with the ethylene at a temperature from 750° to 850°C.

REPLACEMENT SHEET

Date : 16 JAN 1997

THIS SHEET HAS BEEN
REPLACED

PRODUCTION OF ETHYLTOLUENE

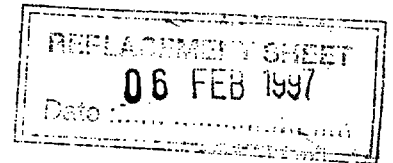
Abstract

Ethyltoluene is produced by ethylating toluene in the presence of a ZSM-5 catalyst of controlled acidity and diffusivity to produce an ethyltoluene isomer mixture which is high in the content of the meta isomer and very low in the ortho isomer. The weight ratio of the meta isomer to the para-isomer is at least 1:1, preferably at least 1.2:1 while the ortho isomer is kept below 1.5%, preferably below 0.5%. The product ethyltoluene may be dehydrogenated to form polymerization grade vinyl toluene.

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PRODUCTION OF ETHYLTOLUENE

Abstract

Ethyltoluene is produced by ethylating toluene in the presence of a ZSM-5 catalyst of controlled acidity and diffusivity to produce an ethyltoluene isomer mixture which is high in the content of the meta isomer and very low in the ortho isomer. The weight ratio of the meta isomer to the para-isomer is at least 1:1, preferably at least 1.2:1 while the ortho isomer is kept below 1.5%, preferably below 0.5%. The product ethyltoluene may be dehydrogenated to form polymerization grade vinyl toluene.