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International and Russian Methods of Synthesis and Use of Pyromellitic acid Dianhydride and Tendencies of Their Development (Review)

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Annotation: **Pyromellitic Dianhydride (PMDA) is a raw material for heat resistant polyimide resins, films and coatings.Methods of pyromellitic acid dianhydride synthesis, its properties, use in the industry are in detail considered and structured for the first time herein as well as a possible tendency of these method development is estimated.**

Key words: Pyromellitic acid, Pyromelliticacid dianhydride, Tetraalkylbenzene, Durene, isodurene, xylene, cumene, pseudocumene, tetramethylbenzol.

The fast development of aircraft industry, rocket building, astronautics, nuclear power, electronics industry, radio engineering and other technics fields demands polymeric materials of high durability, thermal stability, resistance to nuclear and radiation, elasticity and durability. Intensive researches in this field resulted in a synthesis of a new class of cyclopolymers–polyimides[1], with the above physical and mechanical properties.

The main raw materials for high quality polymeric materials are dianhydrides of various aromatic, heteroaromatic and aliphatic acids, and also diamines with a similar structure[2].

A huge range of polyimides, based on a great number of tetracarboxylicacid dianhydrides is synthesized and characterized by the present time, but polyimides of dianhydrides of pyromellitic(1), diphenyloxidetetracarboxylic(2), benzophenonetetracarboxylic(3), perylene- 3,4,9,10 – tetracarboxylic (4) acids (Scheme 1) are used in practice more often. This paper contains international and national methods of pyromellitic acid dianhydride synthesis most used in practice 1.

Pyromelliticdianhydride (PMDA) 1 is colourless crystals with fusion temperature of 287ºC, boiling temperature of 397ºC; dissolved in acetone and dimethyl form amide; under moisture it turns into monoanhydride, and pyromellitic acid (PMA). Pure pyromellitic dianhydride1 is non-degradable at heating to 583-603 K [3].

DuPont (USA) approved its semi-industrial production for the first time in 1960. Later Hexagon (USA) approved the production of this

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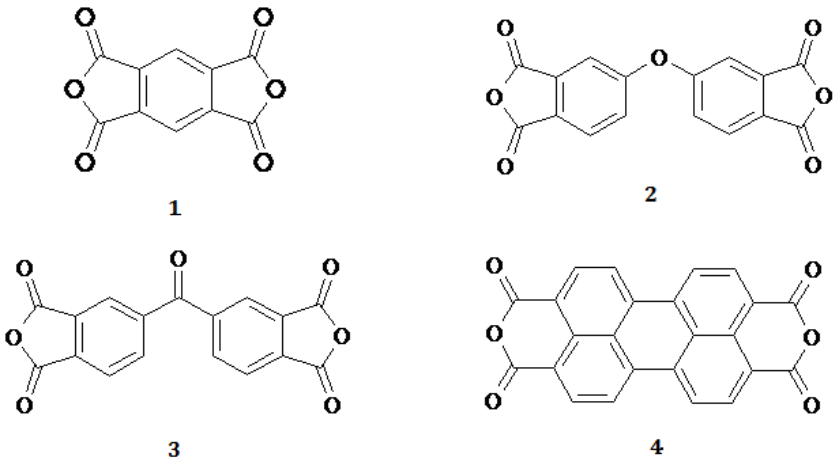


Scheme 1. Dianhydrides of pyromellitic**(1)**, diphenyloxidetetracarboxylic**(2)**, benzophenonetetracarboxylic**(3)**, perylene- 3,4,9,10 – tetracarboxylic**(4)** acids

product under the similar technology. In 1964 these two companies received 181 tons of dianhydride1. Later other largest companies were involved to the technology development and production[1].

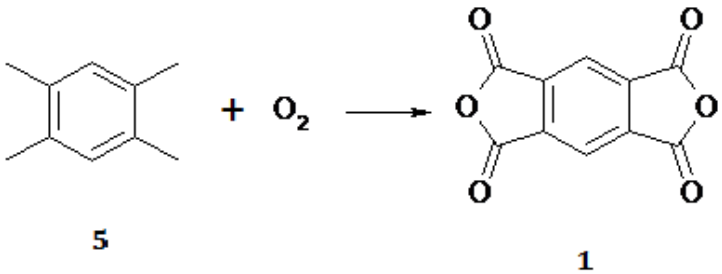
Now PMDA synthesis is based on 3 main methods:

a) Vapor phase processes of oxidation of 3,3',4,4'– tetraalkylbenzenes (mainly durene) at 390-450°C using vanadium - titanic and other catalysts[4, 5, 6].

b) Two-phase processes of oxidation of 3,3',4,4' - tetraalkylbenzene (mainly durene). At the first stage, oxidation is fulfilled with O_2 - gas (air) in aliphatic carboxylic acid (CH_3COOH) with cobalt catalyst, at the second stage, oxidation is completed with nitric acid[7, 8, 9].

c) Liquid-phasep rocesses of oxidation of 3,3',4,4'- tetraalkylbenzene O_2 - gas (air) in the acetic acid with catalysts - heavy metal salts of variable valency and halogencompounds at 120-220°C. Catalysts Co - Mn; Co - Mn - Zr, HBr promoters, tetrabromethane, mixture of HBr - HCl[10, 11] are used more often.

The most common industrial method of pyromellitic dianhydride synthesis is the process based on catalytic oxidation of durene**(5)** with air (Scheme 2):



Scheme 2. Catalytic oxidation of durene(5)

The process is usually spent at temperature of 410ºC - 450ºC, durene concentration in mixture with air 0,1-0,2 % (v), volume speed of durene supply - an air mix 6000-15000 $hour^{-1}$.

Catalysts of vapor phase oxidation of durene of numerous types, consisting of an active base, a co-catalyst and a carrier are developed by the present time. Vanadium pentoxide is used as an active base in all cases. Usually an active base with vanadium pentoxide contains lowest vanadium oxides. Oxides of tungsten, phosphorus, tin, titan, silver, molybdenum, copper, yttrium, niobium, and etc are used as co-catalysts. Poor-porous aluminium oxide, silicon carbide, titanium

oxide, aluminium silicates, and et care used as carriers. This technology is constantly improved that decreases the productprice.

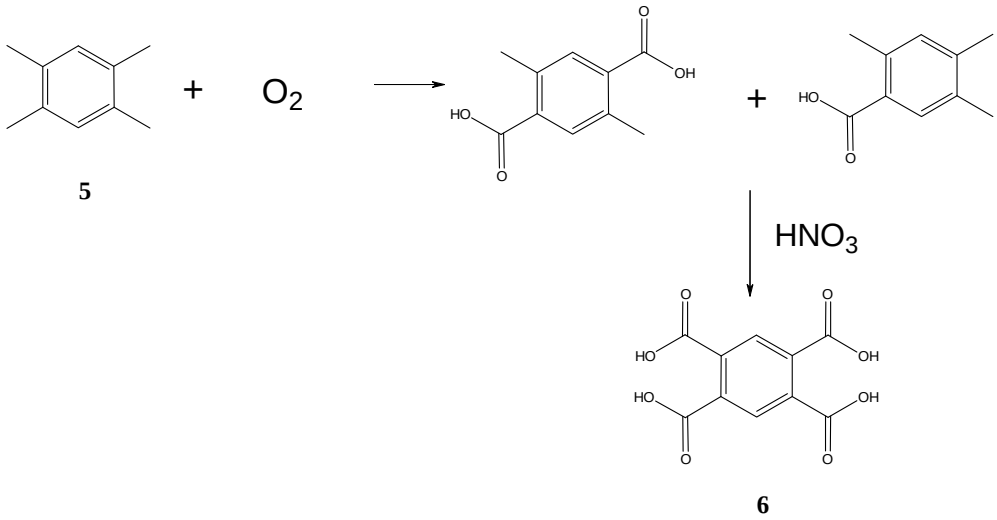
Products of the reaction of vapor phase oxidation of durene **5** include other than pyromellitic dianhydride **1** compounds of partial durene oxidation and its deeper oxidation. Benzenecarboxylicacids, their anhydrides, derivatives of benzaldehyde, phthalide, phtalan, duroquinone are found among products of incomplete oxidation with preserved carbon skeleton. Maleic, dimethylmaleic, citraconic and phthalic anhydride, trimellitic acid, acetic acid, formaldehyde, carbon oxides are found among the deeper oxidation products.

Basing onthe technology specifics and essence for PMDA synthesis by pseudocumene condensation with formaldehyde,product condensation hydrocracking, followed by durene release and durenevapor-phase oxidation to pyromellitic dianhydride**1,**the conclusion can be made that currently the process almost reached perfection and the further product cost can be reduced basically onlyby increasing the industrial plant capacity.

Basing on the literature[10, 11], liquid-phase methods of PMDA synthesis testify that mostly they are similar and different only by the catalyst compound at the oxidation phase (Co - Br; Co - Mn - Br; Co - Mn - Zr– Brandetc) and reaction methods maintaining acatalyst activity by adding a proton acid(HBr)oran acid reagent(CCl_3OOH) stronger than acids of tetraalkylbenzene oxidation products.

In general, a liquid-phase of PMDA synthesis is promising as this technology can be used by a single scheme for the synthesis of other dianhydridesof aromatic acids.

The two-stage PMDA synthesis by tetraalkylbenzene oxidation at the first phase of O_2–with gas (air), at the second phase – with nitric acid[7, 8, 9] (Scheme 3) had been widely used before, but in recent years because of competing vapor phase and liquid phase processes, its use decreased, however not stopped yet.



Scheme 3. The two-stage PMDA synthesis

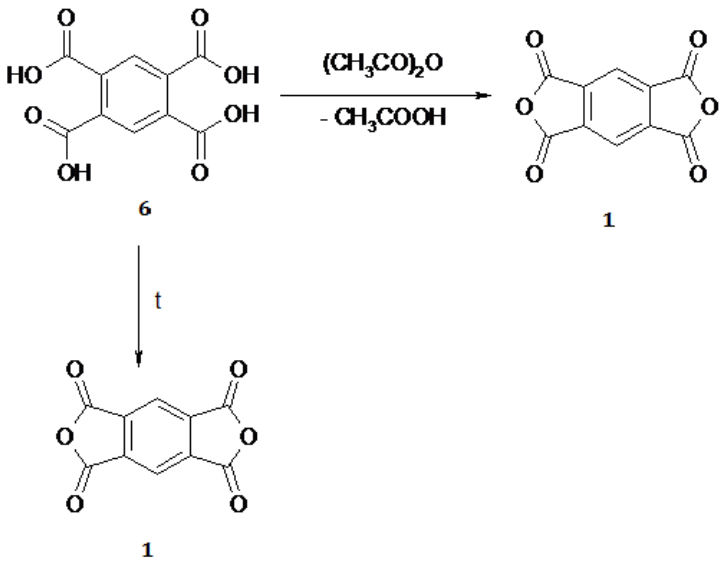
Their use was decreased because of certain disadvantages:

a) Formation of large amount of intermediate difficult-to-separate products;
b) Formation of large amount (10%) of nitro compounds, leading to a product coloration;
c) Formation of explosive compounds;
d) Equipment destruction caused by corrosion;
e) A complex process scheme associated with the need of regeneration of two corrosive active reagents (CH_3COOH and HNO_3).

However, an oxidation with a nitric acid

quite successively competes with a vapor phaseoxidation because of higher yield of the desired product.

Pyromellitic acid **6** can be *anhydridized* by chemical dehydrating agents (usually, aceticanhydride) and thermally (Scheme 4). An hydridization with an acetic anhydrideis technically unacceptable due to the consumption of equimolar amount of the latter (CH_3COOH is formed). Some methods of thermal anhydridization were tested: sublimation, heating under nitrogen and with high-boiling solvents. An hydridization is more rational in high-boiling solvents, improving heat dissipation condition.



Scheme 4. Anhydridization of pyromellitic acid **6**

Anhydridization begins at about 180-190°C, violently proceeds at220-240°C and finishes within 20-30min.Water vapor are removed inthe form of pseudoazeotrope with diphenylseparated from water after condensation and recycled into the process. PMDA is to be washed with boilingdioxane (~4 weight parts per1 weight part of PMDA) and dried at 100-120°C and a residual pressure of 200-300 mm Hg for 10-15hours. PMDA outputis 92-93% of theoretical.The obtained dianhydrideis melted at 286-287°C,its acid number-1026 (calculated 1027), the content of nitro compounds is in significant (traces)[12].

Raw materials for the pyromelliticdianhydride synthesis

Now a days 3,3',4,4'-tetra-alkylbenzoles are used as raw materials to get PMDA, (mainly, durene) released from petroleum refining products or synthesized from hydrocarbonaceous raw materials by the following methods:

1) Durene release from C10 and C9-C10 fraction (after disproportionation or isomerization);
2) High-boiling methylation (300-350°C) of p-xylene or pseudocumene by methanol on aluminosilicate catalysts;
3) Catalytic alkylation of p-xylene or pseudocumene by ethylene orpropylene;
4) Pseudocumene condensation with formaldehyde and di-pseudocumene-methane formation and the further hydrocracking in to pseudocumene and durene;
5) Chloromethylation of p-xylene or pseudocumene.

The above methodsare complex and expensive. Especially it concerns to atechnology of the pure durene preparation from aromatic concentrates of the petroleum refining with a high content of difficult-to-separate alkylaromatic hydrocarbons (prehnitene, isodurene, isomersdiethyl -anddietylmethyl benzole et al).

One of durene concentrate sources is a C_{10} aromatic fraction contained in benzene of

catalystre forming (about1%). So up to 0.15 %wt. of durene can be released from high-aromatic reforming benzene. A possibility of C_9–C_{10}hydrocarbon fraction trans formation into durene by disproportionation[13] and isomerization was studied in order to increase the desired product yield. However, since these reactions are reversible, reactant concentrations are closerto the thermodynamic equilibrium during these reactions using specific catalysts. This phenomenon complicates increasing in the durene isomerization yield. Thus, by the experimental data, the durene yield was increased twice and brought to 15.7%, followed by extraction ofthe low-temperature crystallization into theraw material (durene concentrate).

During isomerization of the mother solution on the silica-alumina catalyst (T =370°C), the durene concentration in the reaction products can be increased from 2% to 13% of weight. But even usingthis combinedprocess, the durene yield does not exceed 33%. The fractionof aromatic hydrocarbons with adistillation temperature of160-177ºCobtained from benzene of catalytic reforming, consists of:

a) Ethyltoluene-16% by weight;
b) Mesitylene- 24% by weight;
c) Pseudocumene-48% by weight;
d) Hemimellitene -12% by weight.

The use of an alum-silicate-molybdenum catalyst (1% MoO_2) at T = 425ºC, P = 80 kg/cm^2, WHSV of 1.0 hr - 1 and circulating of hydrogenous gas of 1000 m_3/m_3 of raw materials increased durene content in the reaction products up to 32.0%. This is confirmed by experimental results shown in Table 1 (% wt).

Table 1. The result of the alum-silicate-molybdenum catalyst use

Aromatic Hydrocarbons	Raw Materials	Product
C6 – 7	-	5,8
C8	-	24,5
C9	100	40,3
C10	-	18,4
C11	-	3,0
C 10 aromatic hydrocarbon compound	-	
Durene	-	32,0
Isodurene	-	64,0
Prehnitene	-	4,0
Paraffin and naphthenehydrocarbons	-	8,0

The above allows to conclude that the content of the side products (non-target) obtained by the above-described method from the fraction boiling at 160-177ºC is large enough(% concentration, wt: isodurene 64,paraffin and naphthenic hydrocarbons 8.0, prenitol–4.0), which reduces the efficiency of the proposed method. Nevertheless, some foreign companiessawan opportunity for the future increase the durene release by his separation from heavy petrol.

Sothe installationlaunch to produce synthetic benzene by Synthetic Fuels Corp was reported in 1982, inMontuno, New Zealand. Benzeneis derived from natural gas via methanol, using a zeolite technologyof Mobil Oil.The formed heavy petrol flow contains up to 50% of durene. Specialists believe that up to 30% can be recovered without significant investments that initially will be 5-10 thousand tons /year, and further 30 thousand tons /year[1].

The Ministry of Energy of New Zealand negotiated with local and foreign companies (including Mitsubishi, Mitsui, ICI) on cooperationin the field of technology for durene separation and pyromelliticdian hydride production.

An agreementon project of durene separation from heavy petrol and commercial deals with other companies was signed between the New Zealand Government andICI Syntec Ltd,a subsidiary companyof ICI New Zealand Ltdand Applied Chemistry Ltd. In addition, the company planned toset up production of pyromellitic dianhydride (designedup to 40 thousand tons / year). Data onits production have not been reported, but using these raw materials the cost price of pyromellitic dianhydride was assumed to be significantly lower than other companies.

Similarly, the studies on durene synthesis were conducted at the State Research Institute of Chemical Technology, Severodonetsk (Ukraine). Experimental durene batches were used by All-Russian Research and Project of Monomers (Tula) to test the technology of pyromellitic acid bya liquid-phase catalyticoxidation (180 - 210°C) in CH_3COOH medium. Pyromellitic acid PMA was turned into PMDA with total yield of 88- 91% of theory by thermal dehydration.

Durene synthesis by methylation using methanol

A methyl group can be introduced in to the aromatic ring by methylation reaction and thus it will synthesize various polymethyl benzenes. Methanol, dimethyl ether, methyl halides and other reagents can be used to add the methylgroup. Usually methanol is an economically beneficent ethylating agent.

The conditions and results of the studies of different catalysts to use them for the synthesis of tetra-alkyl-substituted benzenebymethylation with pseudocumene methanol, xylene isomers and other alkyl-substituted aromatic hydrocarbonsare stipulated in the papers[14, 15].

The authors of the paper [14]found that aluminosilicate catalyst was quite active for this reaction. Methylation goes onwith a significant speed at 300-450°C. The substitution in the benzene ringis in accordancewith the orientationrules in presence of alumino silicatecatalyst at arelatively low reaction temperature (300°C) when a reaction rateof isomerization of initial and obtainedhydrocarbonsis low[15].

The following results were obtained during pseudocumenemethylation(300°C, 0.5h, molar ratio ofmethanol torawmaterials 2- 1:1):

Tetramethylbenzoene yield21.1wt.%

Tetramethylbenzene compound:

a) Durol58.4wt.%:
b) Isodurene 23.7wt.%:
c) Prehnitene 17.9wt.%:

These data show that under these conditions, the yield of tetramethylbenzenes is very lowduring methylation and reaches 21.1%. Thus the content of the desired product (durene) is 58.4%.

The maximum dureneyield atthe above process of durene synthesis by catalytic methylation of aromatic hydrocarbons C_9reaches 73.8%.

Disadvantages of the aboveprocess of durene synthesis include fast coking of the catalyst, significant methanol losses (10-20% of the original), formationof a large number of side and intermediates products of alkylation, isomerization, requiring their recycling or disposal. This in turn necessitates the use of a partitioning scheme (rectification) of complex mixtures, followed by separation (2-foldcrystallization) of the desired product.

The yield of tetra-substituted benzeneisomersis increased due tothe disproportionation reaction or the temperature rising to400°C or morefor convertingof penta-andhexa-substituted benzene into tetra-substituted isomers due toa dealkylation reaction.

Complexity and multistaging of the process scheme, a relatively low yield of the desired product–durene~ 70% and significant irreversible methanol losses of 285kg per a ton of C_9aromatic hydrocarbon suggest that the costsfor production of raw materials –durene for synthesis of pyromelliticacid and its dianhydride will be high enough that will increase incost of PMDA and polyimide based on it.This is confirmed by the production data. Thus, for example, a texisting production, the durene synthesis costs H"48-50% of costs of PMDA synthesis.

To reduce energy and raw material costs in the durene production, All-Russian Research Institute of Organic Synthesis (Moscow) developed a continuous process for synthesis of durene and pseudocumene from p-xyleneby vapor-phasemethylation of the latter with methanol at 430-440°Con the catalystIC–28–2–3.The reactionunitis testedin the experimental conditions and formed in two versions:

a) A divided unit with different gas flow, each section is a separatereactor, turned on sequentially forming a cascade;
b) Avertical shelf unit, each shelf is a section with coils-receivers located between, consuming the reaction heat.

In the reactor according to the first option, the catalyst is located in an annularspace ("basket"). To mitigate the process conditions and uniform temperature distribution, the catalyst is diluted with inert material in a ratio of 1:3.P-xylene and methanol fresh and recycled are heated in a tube furnace to 400- 410°C under a pressure of 2.5-2.6 MPa.

A mixture of source reagent vapors passes through a catalyst layer in the sections at 430-440°C.The methylation reaction proceeds under these conditions forming pseudocumene, durene and byproducts of thermal-oxidative degradation.

Alkylateis sequentially cooled to 165°Cin heat-recovery boilers and to 45°C in heat

exchanger-refrigerators. The reaction mixture goes under further staging separation with dividing of liquid andgas-vapor products.

Alkylateis separated in the rectification unit consisting of four columns, sequentially emitting light fraction of methanol and dimethylether followed by sequentially emitting of p-xylene, pseudocumene, durene and resinousside products.

Durene is purified -raw product from isodurene and other by products with similar boiling temperature- by crystallizationin methanol at 55-63°C. Durene suspensionin methanolis separated in acentrifuge. The isolated wet dureneresi due containing 7-10% of methanolis melted and the residual methanol is distilled off.

The above process of combined synthesis of durene and pseudocumene from p-xylene exceeds the earlier discussed synthesis of aromatic fractions of durene C_9using zeolite catalysts by technological and economic indicators.

The advantage ofthe technology developed by All-Russian Research Institute of Organic Synthesis is in the increased selectivity of the gas-phase methylation of p-xylene with methanoltothree- and tetra-methylbenzenes (pseudocumene and durene).

An improved process fordurene and pseudocumene synthesis developedby All-Russian Research Institute of Organic Synthesis is characterized not only bytechno-economic andenvironmental benefits, but certain disadvantages including high temperature of alkylation process(430-450°C) andpressure (2.5 - 3.0 MPa).

High temperature inevitably leads to thermal catalytic decomposition of raw materials (10%), formation of high (resinous) products that reduce catalyst range and impede alkylate separation.

High pressure of alkylation process increases the equipment cost

Oxidation reactor structures are designed in two variants and under a frequent catalyst regeneration cause complications during their operation.

In connection with the above, the need to develop more cost-effective, low-temperature technology for production of raw materials for PMDA synthesis and its technical and economic comparison to the above vapor phase processis obvious.

However, the polyimide production can be provided with monomer raw materials not only by an improved technology for raw material production for PMDA (dureneor2,5-diisopropyl-p-xylene), but also by replacing the high temperature vapor phase oxidation process(400-450°C) to PMDA, developed by All-Russian Institute of Oil and Chemical Research fora more economical liquid-phase oxidation process (T≤200°C), which provides higher PMDA yield from 65% to ≤ 90%.

Preparation of 1,2,4,5-tetraalkylbenzene by alkylation of p-xylene and pseudocumene

Because of the durene deficiency, syntheses of alternative petro chemicals used as raw materials are developed for synthesis of pyromellitic acid and dianhydride on its basis. These raw materials include products of alkylation of xylenes or pseudocumene with ethylene or propylene in presence of anhydrous $AlCl_3$, namely 5-etilpseudocumene; 2,5-diethyl-p-xylene; 5-isopropyl pseudocumene; 2,5-diisopropyl-p-xylene, respectively[16].

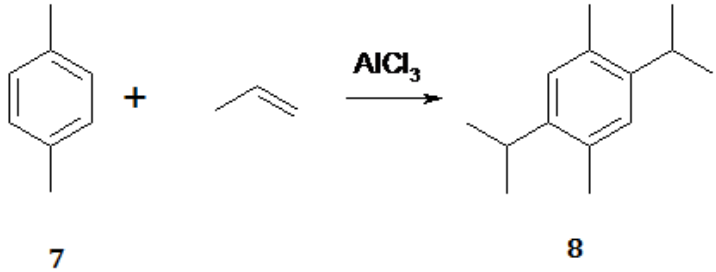
Alkylation of p-xylene and pseudocumene using olefins with Friedel - Crafts catalysts of tetraalkylbenzene cause seem veryinteresting in recent years.

This interest is associated with durene deficiency, a high yield of tetraalkyl benzene comparing to other processes (95%) containing 85% of isomer 1,2,4,5, as well as with the fact that ethylene or propylene are considerably cheaper than methyl chloride used in methylation of aromatic hydrocarbons.

Selective alkylation of p-xylene with propylene forms 1,4 - dimethyl - 2,5 - diisopropyl benzene **8**,as shown in Scheme 5.

The process is going at low temperatures (-10 to -70°C) with aluminum trichloride(0.03 -0.3mol pera mol ofp-xylene) [17]. Alkylationmay be carried outat higher temperatures(30-60°C)with aluminum oxide adding borontrichloride. M-xylene or itsconcentrate[18] can be alkylated in the similar way. As a result of alkylationof pseudocumeneorxylene, 1,2,4,5-tetraalkyl benzeneare formed which give PMC after oxidation.

Some foreign companies have patented



Scheme 5. Selective alkylation of p-xylene

methods for the synthesis of alternative sources of raw materials to solve the problem how to simplify the technology and to reduce the cost of petrochemical raw materials for PMDAsynthesis instead of durene.

Thus, accordingto the U.S. Patent[19], a method is offered to obtain 1,4- dimethyl -2,5 -diisopropyl benzene **8** by alkylation of p-xylene **7** with propylene using a catalyst based on heteropoly acid and/or its salts.The catalyst may contain any heteropolyacid or itssalt, e.g. dodecasilicotungstic acid ($H_4SiW_{12}O_{40}$) dodecaphosphotungstic acid ($H_3PW_{12}O_{40}$) dodecaphosphomolybdic acid ($H_3PMo_{12}O_{40}$) dodecagermanotungstic acid ($H_3GeM_{12}O_{40}$) anddodecagermanomolybdic acid (”$_3$Ge“>$_{1240}$). Compounds obtained by partial orfull substitutionof hydrogen atoms in these heteropoly acids with metals oramines can be served examples of use of heteropolyacid salts. Silica gel, titanium oxide, activated carbon, etc can be usedas a carrier. Impregnation can be used to obtain the heteropoly acid-based catalyst and/ orheteropoly acid salt-based catalyst.Quantityof heteropoly acid may vary from1 to 50% in the carrier of the total catalyst weight. As for the reaction conditions, a molar ratio of propylene and p-xylenemay vary 1,0-5,0; a reaction temperature may vary from70 to 200°C; an operating pressure may vary from normal pressure to10 kg/cm^2.If a reactor is used for continuous reaction, initial materials can be fed into the reaction zone with a velocity of 0.1-10 hour^{-1}(wt. unit/hr).

The main reaction product –dimethyldiiso propylbenzol. The reaction solution containsun reacted initial materials and by products such as dimethyliso propylbenzol and dimethyltriiso propylbenzol. Dimethyldiisopropylbenzol containsisomers and 1,2,4,5-dimethyldiisopropylbenzol. Regardless of thereaction solution compound, the desired product can be crystallized and purified tothe desired quality.But the concentration of1,2,4,5–dimethyldiisopropylbenzolin the reaction productis at least 60wt.%, indicating a need for increased costsat the product isolation andpurification. The reaction product is offered to be treated to separate the catalyst and other undesirable components, followed by crystallization anddistillationof the reaction solutionprior to crystallization. Distillation at a temperature of 150 -300°C should ensure separationof dimethyldiisopropylbenzol from other factions.

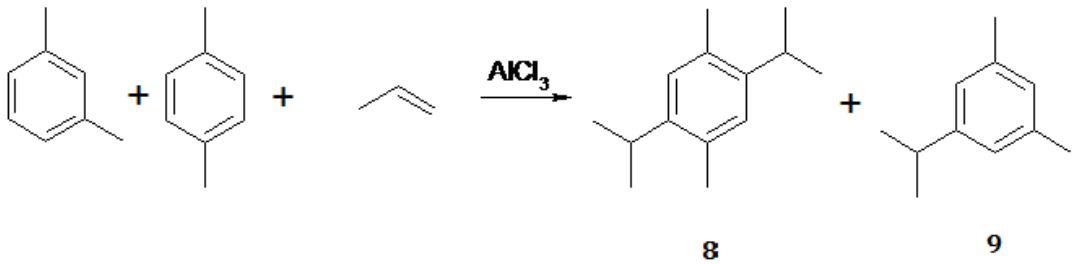
Alkylation products content significant amount of side compounds, indicating a low yield of the desired product andcomplexity of its separation circuit. The lack of data about a possibility (if any) of regeneration orrecycling of the complexcatalyst based onheteropoly acidsor their salts does not allow to make an unambiguous conclusion about the effectiveness of the proposed catalyst and the method as a whole.

AnotherU.S. patent[20] offers a method for synthesis of pyromelliticdian hydride from pseudocumene by alkylation with propylenein presence of an hydrous HFat 150°C. A ratio of pseudocumene to propyleneis 1: 1.1-2(better 1:1.5). A mixture of 2,4,5–trimethylcumene, 3,5 -and 3,6–diisopropylpseu documene is prepared as a result of alkylation. The mixture isoxidized with O_2 -containing gasat 100-500°Cin presence of V_2O_5 catalyst, applied onan inorganic carrier- Al_2O_3. Benzenepolycarboxylic acid isomers are oxidation products. An isomeric mixture can be turned

intothe desired product – pyromellitic dianhydride by decarboxylation of by products at high temperatureof 270-400ºCand a pressure below atmospheric.

This method has advantages comparing to known processes (throughd urene) regarding the useof a new moreaccessible raw material - pseudocumene. At the same time, the use of volatile hydrofluoric acid as a catalyst (aggressive product) during the alkylation as well asan inevitable formation of isomeric mixtures of polyalkylenebenzol acids partiallydecarboxylated undervapor phase oxidation (400-500°C) and thus significantly reduce the process efficiency. Furthermore, free(unbound) hydrofluoric acid (HF)in the reaction medium requires the expensive equipment of alloy steels and alloys, and necessary measures to ensure safe operation conditions for staff.

A synthesis method for 1,3-dimethyl- 5 – isopropyl**9** andtetraalkylbenzenebyalkylationof xylene isomer mixture with propylene in presence of$AlCl_3$at low temperatures of the alkylation process 45-55°C[21] is shown in Scheme 6.



Scheme 6. Alkylationof xylene isomer mixture

The proposed method includes:

(a) contacting of xylene and dimethyldiisopropyl benzolmixturein presence of aluminum chloride for 7-12 hours at 45-55°Cat a molarratio of xylene anddimethyldiisopropylbenzolfrom65:35to 75:25 anda xylenemixture consisting of at least 60 wt %of m-xylene, 0-2wt% o-xylene and the balance of p-xylene;

(b) Adding of propylene intoa mixture (a) at a molar ratioof propyleneandxylenedimethyl diisopropylbenzolinitially added for astage (a) at a level of 0.85:1.0 – 1.05:1.0while maintaining the temperature between 45-55°C within 50-80 minutes;

(c) Separation of dimethylisopropyl benzolanddimethyldiisopropylbenzolfrom the reactionmixture.At the stage (c) dimethylisopropylbenzolcontains atleast 97wt%1,3-dimethyl1-5of isopropylbenzol.

Xylene mixturemainly consists of 68wt. %m-xylene and 32wt.%p-xylene. A partof dimethyldiisopropylbenzol separated at the stage (c) is used as a reactantat the stage(a). At the stage (c) dimethyldiisopropylbenzol contains at least 80wt.%1,2,4,5-tetraalkylbenzene.

The end reaction product contains1.5÷0.4molof dimethyldiisopropylbenzolper molof dimethylisopropylbenzol.

A method forsimultaneous(combined) preparation of mono- anddiisopropyl-xylene isomers by alkylation of xylene fraction in presence of Friedel-Crafts reaction catalyst[22] is the closest bythe technical nature.

The proposed method is based onthe alkylation with propyleneof xylene fraction enriched to 68% with m-xylene, in presence of$AlCl_3$ with preparation of an isomeric mixture ofmono- anddiiso propylxylene. This method allows to regulate anisomer ratioin a mixture ofmono- and diisopropylxylene by additional prior separation of alkylation products into a fraction with a high content of diisopropylxyleneisomers (fraction-2)and a fraction with a high contentof monoisopropylxylene isomers (fraction- 1).

Fraction 2is to be re-alkylated with xylene in presence of Friedel–Crafts catalyst for 7-12 hours at 45-55°C, followed by treatment of the obtained mixture with propylene for 50-80 minutes at 45-85°C. Alternatively fraction- 2 is mixed with xylene in a molar ratio of 40:60-60:40 in presence of$AlCl_3$at 70-80°Cfor 3 hours, followed by an additional

treatment of the obtained mixture with propylene at45-60°Cto themolar ratioof monoisopropylxylene to diisopropylxylene45:55-35:65.

The main disadvantageof the proposed methodis thatthe use ofxylene fraction complicates an isomeric mixtureof alkylation products, its separation to alkylbenzol (2,5- diisopropyl- p-xyleneor 5-izopropylpseu documene) is quite complex and requires considerable costs.

To separate pure 2,5 –diizopropylxylene – an alternative raw material for PMDAsynthesis from this complex isomeric mixture is difficult, asthe boiling point of isomeric components are very close, so the method is complicated with additional stagesof re-alkylation, isomerization, trans alkylation.

The patent [23] stipulates a method of synthesis of tetraalkylbenzene(5-isopropylpseu documene and 2,5–diisopropyl- p-xylene) whereby alkylatedpseudocumeneormonoisopropyl- p-xyleneinone stage at 70-90°Cin the presence ofa catalyst$AlCl_2 \cdot H_2PO_4$ until a conversion of initialhydrocarbon 40-90%, and accumulation inalkylateof individual5-mono-isopropylpseu documeneor 2,5 -diisopropylbenzene,at least 50%, followed by separation of alkylate and concentrateof isomers of monoisopropylpseu documene or diisopropyl- p-xylene, subjected to exposurein inert gas atmosphere in presenceof $AlCl_2 \cdot H_2PO_4$at 60-90°C for2-6 hours to concentration of 5-isopropylpseudocumene or 2,5 -di-isopropyl- p-xylene,at least 95%.

This methodcan simplifythe synthesisof two alternativepetrochemical products,their oxidation leads to the formationof pyromelliticacid andthe further thermaldehydration of the latter-to obtain pyromelliticdianhydride.

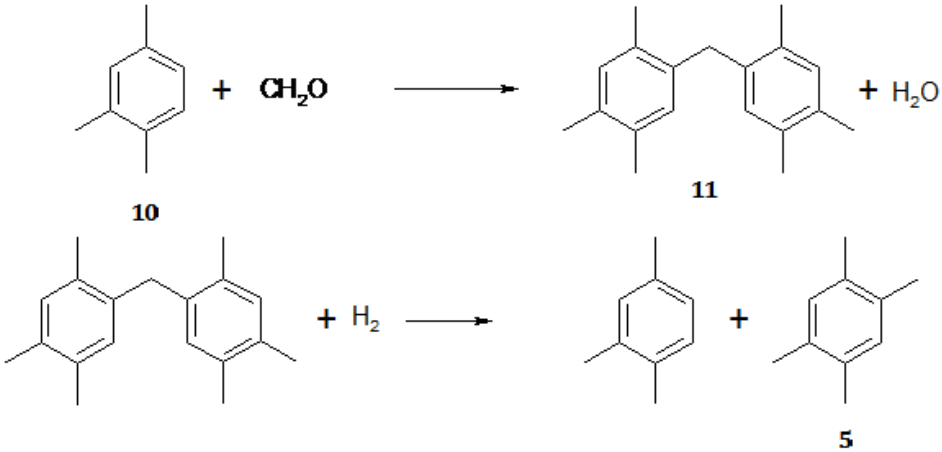
According to thesedata, the synthesis of1,2,4,5-tetraalkylbenzene by alkylationof pseudocumeneor p-xyleneis believed to be one of the effective methods of raw material obtaining forPMDA synthesis.

Durenesynthesis by condensation

The industrialprocess fordurene **5** synthesis by pseudocumene **10** condensation with formaldehyde, followed by hydrocracking of forme dalkyldiphenylmethan **10** (dipseudocu methane) designed by Shell Development Company[24].

The chemical processcan be represented bythe reactions shown in Scheme 7.

The reaction of pseudocumene condensation with formaldehyde for dipseudocume thane synthesis is studied inpresence of p-toluene sulfonic acid(paraformaldehydewas used) and



Scheme 7. Durene**5** synthesis by pseudocumene**10** condensation with formaldehyde

sulfuric acid (formaldehyde isintroduced in the form of formalin).

Table 2 shows the yieldand compound of pseudocumenecondensation productsobtained inpresence of p-toluenesulfonic acidand sulfuricacid.

P- toluenesulfonic acid is better as a catalyst because the process proceeds with greater selectivity and higher yield of dipseudocumethane than in presence of sulfuric acid.

Table 2. Yields and compounds of the pseudocumene product condensation.

Reagents and Catalysts	Paraformaldehyde and toluene sulfonic acid	Formalin and 88% sulphuric acid
Synthesis conditions:		
Temperature, °!	90	90
Contact time, h	4	4
Molar ratio of pseudocumene and formaldehyde	2 : 1	2 : 1
Catalyst amount, wt. % perpseudocumene	12,5	25,0
The yield of hydrocarbon layer, wt. % per pseudocumene	105	108
Hydrocarbon layer compound, %		
Dipseudocumethane	78,0	50,0
Pseudocumene	21,0	42,6
Deep - condensated pseudocumene products	–	7,0
Formaldehyde	0,4	0,3
P-toluenesulfonic acid	0,6	–
Sulfuricacid	–	0,1
Acid layer compound, wt.%		
P-toluenesulfonic acid	50,0	–
Sulfuric acid	–	49,0
Formaldehyde	7,0	8,0
Water	43,0	43,0

Dipseudocumethane is turned into durene and pseudocumene by hydrocracking over alumocobaltmolybdic catalyst. Dipseudocum ethane decay reaction proceeds completely at 450°C and a partial pressure of hydrogen from 0.5 to 2.0 MPa (5-20 kgf /cm^2); a molar ratio of hydrogen to feed 5 - 6.5: 1, the contact time exceeds 20 seconds. The selectivity of the dipseudocumethane hydrocracking decreases while the contact time is increasing. Increase in the contact timeleads to increased isodurene concentrations, prehnitene concentration remains constant.

Tetramethylbenzene mixture obtained by dipseu docume than ehydrocrackingcontains (in wt.%): durene 80-87; isodurene 5-10;prehnitene8–10. Becauseof asignificant content of isodurene and prehniteneintetramethylbenzenes, special methods are required to separate high purity durene: clearrectification or crystallization.

The total (average) durene yield considering allprocess stages (condensation, hydrocracking and rectification) makes 65% perinitial pseudocumene.

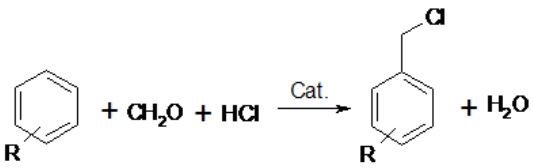
The main disadvantages of durene synthesis from pseudocumene by condensation methodand hydrocrackingare:

1) High energy consumption;
2) A lowdureneyield(65%);
3) A large amount of waste(>1t /tdurene).

Preparation ofd urene by chloromethylation

Chloromethylation reactionof aromatic hydrocarbons (benzene and its alkyl derivatives) has long been known[25]as a methodof an aromatic ring substitution with H_2Cl chloromethylgroup, it was discovered byGrassy and Maselliin 1898(in literature –Blancreaction)and its general scheme can be represented as shown in Scheme 8.

$ZnCl_2$, H_2SO_4, $AlCl_3$8 $SnCl_3$ are used as catalysts more often,and a mixture of hydrochloric acid and formaldehyde as a26-40% solution is usually used for forming CH_2Cl-groups.



where R: CH_3, C_2H_5, C_3H_7, OCH_3,OC_2H_5etc

Scheme 8. Blanc reaction

The raw material synthesis to obtain pyromellitic acid bychloromethylation ofalkyl aromatic hydrocarbonswas reported in the period of 1951-1968 years[12]. Firstlym-xylene, p-xylene and pseudocumene were used as alkylaromatic hydrocarbon. A mixture of hydrochloricacid and

form aldehy deserved as a chloromethylating reagent[12]. The yield of substituteddurene products using p-xylene was 80%, while usingm-xylene-70%.

The yield of monochlormethyl pseudocumeneis 78% by pseudocumenechloro methylation with paraformaldehyde in35-36% hydrochloric acid.

According to the patent[26] pseudo-cumenechloro methylationis carried outat e"150°C anda pressure of 0.5-1.5MPa.1 –chloromethyl-2,4,5–trimethylbenzene obtained this wayis transformed into durene under the at the gaseous phase at150-200°C.

Chloromethyl derivativecan also be recovered with zinc inpresence of hydrochloricacid. Also chloromethylderivatives canbe notrecovered buthydrolyzed to alcohol which by oxidationis transformed into pyromellitic acid.

M.I.Farberovshows in his paper[12] that chloromethylderivatives are formed during chloromethylation of m-or p-xylenewhich, afterhydrolysisto correspondinggly colsorpoly ethers can bedirectlyoxidized topyromellitic acid.

The well-known German company" BergWerkSfer Band" produces PMDA using chloromethylation of p-xylene with paraformaldehy deusinghydrochloricacid and acetic acids.

This process consists of three main stages: chloromethylation, hydrolysisand oxidation. At the first stage, p–xylene ischloro methylated using para formaldehyde and hydrochloric and acetic acids at 70-85°C and0.5 MPa.At the second stage,the obtained dichloromethyl- p –xyleneis saponifiedat 70°C in presence of alkali solution and methanol. The obtained methoxy derivativeis purified by distillation. At the thirdstage, dimethoxy- p – xyleneis oxidized with 20-25% -nitric acid at 190-200°C and2.0MPa.The significant disadvantages of this process are the high unit costof raw materials and reagents.

Duringthe "BergWerkSferBand"'s processto obtainone ton ofpyromellitic acidthe following is consumed: 0.59ton of p-xylene, 0.38 tonof paraformaldehyde, 0.56 tonof hydrochloric acid, 0.25ton of acetic acid,0.45 ton of sodiumalkali, 0.54 ton of methanol and 1.62 ton of nitricacid.

M.I.Farberov *et al*[12] developed the process of PMDA synthesis based onchloromethylatedxylenes, which excludes acetic acid andm-xylene. The process consists of the following stages:

a) Chloromethylation of xyleneat 95-100°C, pressure of 0.2-0.3MPaand separation of1,2,4,5-isomersby recrystallization;
b) Hydrolysis of 1,2,4,5-isomers with an aqueous alkaliforming corresponding glycols and polyethers;
c) Oxidationof hydrolysis products with 20% nitric acid at180°C, pressure of 2.0MPaand 12-fold molar excess.

PMC yield at the oxidation stage is87-93 mol%, and per xylenessource- 65mol%.

Pseudocumene becomes widely available technical product, which canbemore acceptable comparing to xylenes for the three stage synthesis of PMC based on chlormethylation.

Though the durene synthesis technology using chloromethylation reaction has not been developed very well because of significant raw material costs, large amount of waste, a relatively low efficiency of the process and, consequently, higher costs of durene comparing to other processes, however recently, this methodseems interesting because of its possible improvement to a level of competing technologies.

The paper [27], published in 2010, describes the synthesisof raw materials – bis (chloromethyl) xylene **15, 16, 17** for the pyromellitic acid synthesis 6bychloromethylation of xylenes12, 13, 14in an aqueousmedium, using as a catalyst[C_{12}mim] Br.bis (chloromethyl) xylenesbyaerobic oxidationin presence ofcatalyst VO (0A0A)$_2$ / Cu(2 – Eth)$_2$ /DABCOin [hmim]OTfis transformed into pyromellitic acid**6**, dehydratedby heating in presence of aceticanhy dride (Scheme 9).The yieldof pyromellitic dianhydrideis 76.7%.

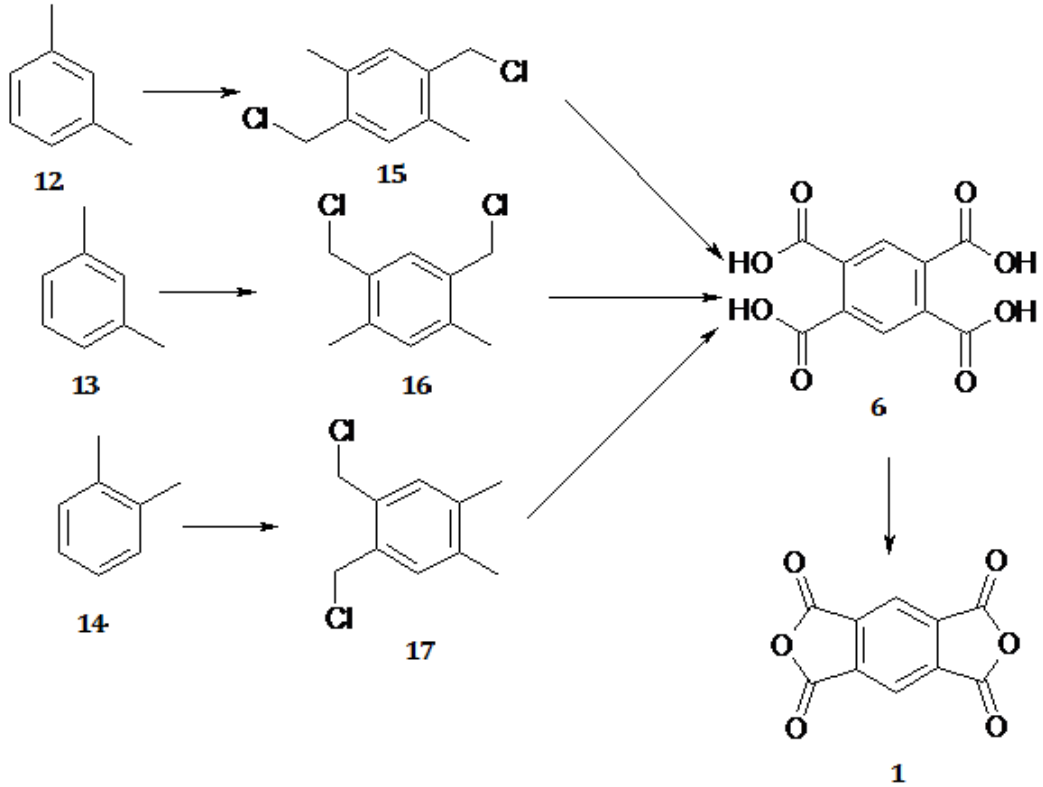
The main disadvantage of durene synthesis by chloromethylationisa large amount of wastes (more thanone t/ tof durene).

The technical and economic comparison of durene synthesis by known methods from different sourcesof petrochemical raw materials, conducted earlier by scientific-research institutes and describedin [b] is shown belowin Tables 3 and4 for anapproximate comparative assessment.

According to the above, thealkylationof fraction C_9 and higher and xylene fraction dis proportionation are characterized by bestindicators

and better efficiency. By these methods, durenecan be synthesized at relatively low operation costs and capital expenditures.

However, taking into account the development of new technologies and improvement of known processes, the comparative technical and economic assessment should be reviewed and specified by the results achieved.



(I) $(CH_2O)_n$, 50% H_2SO_4. AcOH $[C_{12}mim]Br$, HCl, 55°C, 12 hours;
(II) VO $(acac)_2$ / $Cu(2 – Eth)_2$ / DABCO hmimotf, O_2, 120°C, 24 hours;
(III) $(CH_3CO)O_2$, boiling, 3 hours.

Scheme 9. Three-stage synthesis of PMDA(using ionic solvents iLS).

Table 3. Comparison of the main technical and economic indicators of durene synthesis by different methods,%

DureneSynthesis Methods	Annual yield of 100%durene	Capital expenditures	Operat in g costs	Cost price of gram of 100% durene
Alkylation by methanol of fraction C_9 and higher	100	100	100	100
Alkylation of aromatichydrocarbons concentrate of catalytic cracking	100	245	200	215
Isomerization of aromatic hydrocarbons by catalytic cracking	100	400	570	170
Pseudocumene condensation and hydrocracking of condensation products	100	190	240	290
Durene separation from the heaviest part of plat forming benzole	100	480	950	420
Disproportionation of xylene fraction	100	235	290	105

Table 4 . 1 g Durene Production Cost Structure,%

Expenditures	Durene Production					
	By alkylation		Isomerization of aromatics hydrocarbons of catalytic condensation products	Pseudocumene condensation and hydrocracking of forming	By durene separation from heavy part of benzoleplat forming	Bydisproportionation of xylene fraction
	With Methanol of fraction C_9 and higher	cracking Concentrate of aromatics hydrocarbons ofcatalytic cracking				
Raw materials and basic materials	44,9	76,4	102,3	54,1	180,4	45,2
Auxiliary materials	7,0	2,4	6,6	18,7	5,1	14,1
Process fuel	2,5	0,8	1,2	0,3	0,1	0,3
Energy costs	4,2	14,0	20,7	7,3	80,1	51,7
Semi-fixed expenses	34,7	27,0	44,5	15,4	21,6	67,8
Shop expenses	2,3	2,4	5,4	1,3	5,7	6,7
Works general expenses	6,0	6,1	13,8	3,3	14,6	17,2
Total	101,6	129,1	224,5	100,4	307,5	203
Byproducts	1,6	29,1	124,5	0,4	207,5	103
The cost price of one ton of marketable durene	100	100	100	100	100	100

CONCLUSION

The results of the study ofthe existing syntheses of pyromellitic acid dianhydrideshowed the following.

1. This monomeris notmanufactured in Russia. The unit for PMDA synthesis designed and builte arlier(1970-1980years) at OAO "Ufaneftekhim" in 1995ceased theproduction and was later liquidated. Currently, pyromellitic acid dianhydrideis imported.
2. Foreign manufacturersof PMDA("Lonza Liang Chemical Co. Ltd",China, "Hamish Werke*Hüls*", "Gecher Halenge" Germany, "Dupont" USA,"Mitsubishi", "Sumimoto" Japan, "Hatcher" New Zealand) produce PMDA by vapor-phaseandliquid-phase methods of dureneoxidation using vanadium or vanadium-titanium catalysts at the vapor phase oxidation and metalbromide –at the liquid phase oxidation.
3. Currently,the source petrochemical raw materials in PMDA synthesis isdurene or 5–isopropyl pseudocumene derived from pseudocumene under the methods mentioned in the article.

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