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Thorough Elimination of Acetylenic Hydrocarbon Impurities from Various Mixtures

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Acetylenic hydrocarbons are a very undesirable impurity in many instances of polymerisation, oxidation, and other syntheses. The problem of the elimination of acetylene derivatives from various mixtures has been investigated in fair detail: patent data are particularly numerous. This review is based on studies published up to 1970; an attempt has been made to give a systematic account of and to compare the advantages and disadvantages of various methods and procedures for the thorough elimination of the above impurities and certain physical properties of the principal components of the mixtures purified and analytical methods for the determination of the acetylenic hydrocarbon impurities have been examined.
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I. INTRODUCTION

One of the particularly undesirable impurities, which are difficult to remove and which have a significant influence on the polymerisation of monomers and the quality of polymers[1-8], cause explosions in oxygen works[9], and inhibit the oxidation of organic compounds, are acetylenic hydrocarbons (AH). Therefore, the increase in the manufacture of large-scale products of the petrochemical industry such as ethylene, propene, isobutene, halogenoethylenes, isoprene, butadiene, and others, produced by the pyrolysis and dehydrogenation of hydrocarbon raw materials or synthesised from raw acetylene, must inevitably involve the development of effective processes whereby acetylenic hydrocarbons can be thoroughly removed. In particular the polymer industry imposes very vigorous requirements on the purity of the monomers. Thus ethylene and propene used in high-pressure polymerisation and vinyl chloride must not contain more than 0.0005 vol. % of acetylenic hydrocarbons[10-13] and their content in isoprene and butadiene should not exceed 0.0004 and 0.005 wt. % respectively[14]. In the future the requirements which will have to be met by methods for the elimination of acetylenic hydrocarbon impurities from industrial mixtures and by methods for the analytical control of technological processes will naturally become more stringent.

Many procedures have been described for the thorough elimination of acetylenic hydrocarbon impurities from hydrocarbon and non-hydrocarbon mixtures involving various methods. However, so far no review has been published on this practically important problem. In the present review the procedures and methods for the thorough elimination of acetylenic hydrocarbon impurities from various mixtures are described and critically assessed from the standpoint of their suitability in practice.

II. SOME PHYSICAL PROPERTIES OF THE MAIN COMPONENTS OF THE MIXTURES PURIFIED[15-25]

The Table lists certain physical properties of the main components of the mixtures purified and also mixtures of the acetylenic hydrocarbon impurities.

III. METHODS FOR THE THOROUGH ELIMINATION OF ACETYLENIC HYDROCARBON IMPURITIES FROM VARIOUS MIXTURES

The following methods are known for the removal of acetylenic hydrocarbon impurities from various gaseous and liquid mixtures: sorption, distillation, catalytic hydrogenation, catalytic oxidation, catalytic polymerisation, and certain others.

1. SORPTION

The sorption purification methods are based on the enhanced absorption capacity of certain sorbents—liquids, salt solutions, and solid porous materials—in relation to acetylenic hydrocarbons. Therefore three technological processes are usually employed for the purification:
(a) absorption by liquids; (b) adsorption by solids;
(c) chemical interaction between the acetylenic hydrocarbon and the sorbent, i.e. chemisorption.

a. Absorption by Liquids

Acetylenic hydrocarbons and in particular acetylene (A) are comparatively readily soluble in many organic solvents[26-28], in contrast to many other hydrocarbon and non-hydrocarbon compounds. This property of acetylenic

Some physical properties of the principal components of mixtures from which the acetylenic hydrocarbon impurity is removed.

Substance	Mol. wt, M	M.p., °C	B.p., °C (760 mmHg)	Specific gravity relative to air (0°C, 760 mmHg)	Specific gravity of liquid d_4^{20}, g cm^{-3}	Refractive index n_D^{20}	Cryst. temp., °C	Crit. pressure p, atm	Explosion limits in mixtures with air, vol.%	Heat of combustion, Q_{comb}, kcal mole^{-1}	Thermal conductivity, 10^5 cal cm^{-1} s^{-1} deg^{-1}
Hydrogen	2.016	—259.20	—252.78	0.0695	0.0763$^{-258.3}$	—	—239.9	12.8	4.0—74.2	68.77	41.60
Nitrogen	28,016	—210.02	—195.81	0.9673	0.8622$^{-208.4}$	—	—147.1	33.5	—	—	5.80
Oxygen	32.00	—218.83	—182.97	1.1053	1.2489^{-205}	—	—118.8	49.7	—	—	5.89
Carbon monoxide	28.01	—205	—191.5	0.9669	0.8471^{-205}	—	—140.2	34.5	12.5—74.2	68.32	5.14
Methane	16.04	—182.44	—161.58	0.5545	0.3242^{-107}	1.00044°	— 82.1	45.8	5.0—15.0	212.79	7.02
Acetylene	26.04	—80.8^{1277}	— 83.8	0.9073	0.6154$^{-80.3}$	0.00051	35.3	61.6	2.5—80.0	311.36	4.40
Ethylene	28.05	—169.19	—103.7	0.9749	0.5699$^{-103.4}$	1.363^{-100}	9.7	50.9	2.7—28.6	337.28	3.92
Ethane	30.07	—182.81	— 88.63	1.0488	0.5612^{-100}	1.00075°	32.27	48.2	3 2—12.5	372.8	4.31
Methylacetylene	40.06	—104.7	— 23.23	—	0.690 $^{-40}$	—	128	52.8	—	465.1	—
Propene	42.08	—185.25	— 47.75	1.4804	0.6095^{-47}	1.3567^{-40}	91.8	45.6	2.0—11.1	491.82	3.33
Propane	44.09	—187.65	— 42.06	1.554	0.5794^{-40}	1.3395$^{-42.5}$	96.81	42.01	2.4—95.0	530.57	3.59
Diacetylene	50.06	— 36.4	10.3	—	0.7364°	—	—	—	—	—	—
Vinylacetylene	52.08	—138	5	—	0.6876	—	168	50.7	—	—	—
Butadiene	54.09	—108.92	— 4.47	1.8832	0.650°	1.4292^{-25}	152	42.7	2.0—11.5	618.1	—
Dimethylacetylene	54.09	— 32.3	26.97	1.918	0.6906	1.3893^{25}	215.5	—	—	—	—
Ethylacetylene	54.09	—125.72	8.07	—	0.6906	—	190.5	—	—	—	—
Isobutene	56.10	—140.35	— 7.01	1.9336	0.6268$^{-6.6}$	1.3796^{-25}	144.73	39.48	—	647.2	3.08
α-butene	56.10	—185.3	— 6.25	1.9336	0.6182°	1.3777^{-25}	146 4	39.7	1.7— 9.0	649.66	3.08
cis-β-butene	56.10	—138.9	3.72	—	0.6213	1.3932^{-25}	157	41	—	—	2.48
trans-β-butene	56.10	—105.5	0.88	—	0.6042	1.3842^{-25}	157	41	—	—	2.85
butane	58.12	—138.35	— 0.50	2.091	0.5789	1.3600^{-25}	152	37.5	1.8— 8.4	687.94	3.22
Isobutane	58.12	—159.4	— 11.72	2.067	0.5572	1.3503^{-25}	134.9	36.0	1.8— 8.4	686.3	3.12
Propylacetylene	68.12	—106.1	40.23	—	0.6940	1.4079^{18}	—	—	—	—	—
Isopropylacetylene	68.12	—	29.0	—	0.6854°	1.3756	—	—	—	—	—
Ethylmethylacetylene	68.12	—109.3	56.12	—	0.7127^{17}	1.4004	—	—	—	—	—
Isoprene	68.12	—145.95	34.067	2.358	0.6809	1.4216	—	—	1.7—11.5	—	—
α-pentene	70.14	—165.2	29.97	—	0.6405	1.3715	201	40	—	803.4	—
cis-β-pentene	70.14	—151.37	36.94	—	0.6555	1.3828	202.4	40.4	—	—	—
trans-β-pentene	70.14	—140.2	36.35	—	0.6482	1.3793	202.4	40.4	—	—	—
α-isopentene	70.14	—168.5	20.06	2.428	0.648	1.3640	191.4	33.9	—	807.63	—
β-isopentene	70.14	—133.78	38.57	2.428	0.6623	1.3869	191.6	35.3	—	795.7	3.12
pentane	72.14	—129.7	36.08	2.4872	0.6259	1.3576	196.6	33.3	1.4—78	845.27	3.12
Isopentane	72.14	—159.89	27.85	2.4872	0.6197	1.3539	187.8	32.9	1.3—	843.36	2.91
Vinyl fluoride	46.04	—160.5	— 72.2	—	0.853 $^{-72.2}$	—	54.7	53.35	—	—	—
Vinyl chloride	62.49	—159.7	— 13.9	—	0.9730^{-15}	1.38^{-15}	150.4	55	3.65—26.6	17.59	—
1,1-Difluoroethane	66.05	—	— 24.7	—	—	—	113.5	44.4	—	—	—
1,1-Dichloroethane	98.95	— 96.7	57.3	—	1.174	1.4166	—	—	—	—	—
1,2-Dichloroethane	98.95	— 35.5	83.5	—	1.253	1.4448	—	—	6.2—16	—	—

hydrocarbons is used to extract them from a wide variety of complex systems in order to free them from this impurity.

A number of procedures have been developed and proposed for the removal of acetylene from coking gas[29-31], cracking gas[32-34], and gases involved in the partial oxidation[35] and high-temperature pyrolysis[36] of hydrocarbons, which contain it in an amount of 7–10 vol. %. Acetylacetone, methanol, kerosene, acetone, dimethylformamide (DMF), *N*-methylpyrrolidinone, ethyl methyl ketone, butyrolactone, and others are employed as selective solvents. The absorption process is usually carried out in several stages, mainly at temperatures between −30° and −70°C and pressures in the range 10–16 atm. The degree of extraction of acetylene is not more than 97–99%.

Many studies have been made on the develoment of a process for the preparation of ethylene free from the acetylene impurities using selective absorption of the latter. The majority of investigators[32-47] suggest that acetylene be selectively extracted from the crude ethylene or the C_2 fraction obtained from the coking and cracking gases or the gases from the pyrolysis of the hydrocarbon raw material. Acetylene is absorbed from the C_2 fraction by selective solvents at a temperature close to the liquefaction temperature of the mixture and at an elevated temperature. However, ethylene containing about $1-10^{-4}$ vol. % of acetylene, compared with its initial concentration in the mixture of 0.05–1.58 vol. %, could be obtained in only a few cases[43,44,46].

The method of selective absorption by organic solvents is used to eliminate acetylene from halogenated hydrocarbon mixtures. Thus treatment of vinyl chloride containing 0.18 vol. % of acetylene with methanol in a countercurrent absorber yields a product containing only 0.006 vol. % of acetylene[48]. Insignificant amounts of acetylene are removed from its chlorination products by passing the hydrocarbons mixed with a solvent (water, acetone, etc.) continuously through an injector or an ejector[49]. Dimethylformamide, dimethyl sulphoxide, *N*-methylpyrrolidinone or their mixtures have been proposed as selective solvents[50-54] for the separation of gaseous mixtures consisting of 67–85 vol. % of vinyl fluoride, 15–31.5 vol. % of acetylene, and admixtures of other hydrocarbons. However, the vinyl fluoride concentrate isolated contained about 0.8 vol. % of acetylene.

When isoprene containing 1.4 mole % of higher acetylene hydrocarbons is treated with an aqueous solution of dimethylformamide at 0°C, the amount of impurity diminishes only to 1.0 mole %.[55] In addition, many absorption procedures for the extraction of acetylene from various gases evolved in the processing of hydrocarbon raw materials with the aim of concentrating it have been described, but these will not be considered here.

b. Adsorption by Solids

The adsorption of acetylene on artificial zeolites of type 4A and 5A, activated charcoal of type KST, and silica gel of type MSM from gases produced in the oxidation of methane by air and oxygen at temperatures between −78° and +80°C has been investigated[56]. According to the results, zeolites show promise in the extraction of acetylene from gases produced by the incomplete oxidation of methane and in the thorough removal of acetylene from industrial gases, for example ethylene.

A process has been developed for the adsorption elimination of traces of acetylene from air in apparatus employing gaseous and liquid oxygen by means of zeolites of types NaA and CaA.[57-59] A high efficiency of purification is achieved at 20–70°C and when the acetylene content in the initial mixture is not more than 2.4 $cm^3\ m^{-3}$. When the average content of acetylene in air is 0.03 $cm^3\ m^{-3}$, one ton of type CaA zeolites purify without regeneration 9×10^6 m^3 of air and operate for 300 h. However, CaA zeolites have a high regeneration temperature (350°C) and, when the concentration of acetylene in air is about 1 $cm^3\ m^{-3}$, their dynamic activity falls sharply. The adsorption properties of various ion-exchange forms of type A and X zeolites with various degrees of substitution of sodium by the cations of other metals have been investigated[60]. It has been found that the optimal form is a type X zeolite with a low degree of substitution of sodium by transition-metal cations. Together with a high adsorption capacity in relation to acetylene (15.8 cm^3 of acetylene per 100 cm^3 of zeolite), it has a low regeneration temperature (250° to 300°C). Other investigators[61] recommend KSM silica gel as an adsorbent for the same purpose. At temperatures between −100° and −160°C, it absorbs acetylene from the gas stream almost completely. KSM silica gel has been recognised as the best agent for the purification of the ethylene fraction obtained in the low-temperature separation of coking gas[62]. At a gas space velocity of 840 h^{-1} and a temperature of −100°C and below, it absorbs acetylene to the extent of 30–80% and its homologues to the extent of 80–95%. Treatment of liquid ethylene in an autoclave under a pressure of 19 atm at −30°C in the presence of an adsorbent comprising a mixture of alumina gel and silica gel[63] makes it possible to reduce the acetylene content in ethylene from 4.4×10^{-3} to 7×10^{-4}%.

The possibility of the employment of continuous adsorption for the removal of acetylene from vinyl chloride[64-66] and for the selective extraction of acetylene from gases produced by the incomplete oxidation of methane[67-71] has been investigated. When Hungarian activated charcoal with a specific surface of 996 $m^2\ g^{-1}$ was employed and the process was carried out at 20°C, a pressure of 1.5 atm, and a space velocity of about 200 h^{-1}, fractions virtually free from acetylene were obtained.

c. Chemisorption

In order to improve the efficiency and selectivity of the processes for the sorption extraction of acetylenic hydrocarbons from various mixtures, the chemisorption principle, i.e. chemical binding of acetylenic hydrocarbons by sorbents, which usually contain copper, silver, or mercury compounds, has been used in a number of cases.

Numerous studies have been made[72-86] on the selective elimination of acetylenic hydrocarbons from the C_4 fractions with a high content of diolefins, for example butadiene, before the extraction of the latter.

Acetylenic hydrocarbons are chemisorbed from such gaseous or liquid fractions by treatment with an aqueous ammonia solution of copper(I) acetate at temperatures between −10° and +10°C. The acetylenic hydrocarbons then form soluble complexes with copper and remain in solution. They are desorbed by heating the solution to 80–105°C, sometimes using a desorbing gas, for example ammonia[83]. On desorption, part of the artylenic hydrocarbons are polymerised; the high-molecular-weight compounds are separated by passing the solution through a layer of activated charcoal. The acetylenic hydrocarbon impurity (0.15–0.3 wt. %) can be extracted by this procedure only to the extent of 70–95%. It has been stated[80] that, under the purification conditions, butadiene is sorbed by the solution 150 times less effectively than acetylenic hydrocarbons. In order to remove small amounts of acetylenic hydrocarbons from gaseous mixtures, the hydrocarbons are chemisorbed by an ammoniacal solution of copper(I) chloride with formation of copper acetylide precipitates. In particular, the use of this solution for the thorough elimination of the acetylene impurity from vinyl fluoride[8,87] results in an acetylene content in the purified gas not greater than 4×10^{-5} vol. %. With this method of purification, the content of higher acetylenic hydrocarbons in alkenes diminishes from 0.3 to 0.001 wt. %.[88] Acetylenic hydrocarbons are removed from streams of ethylene and butadiene by passing them through a solution of copper(I) chloride in dimethyl sulphoxide[89]. It has been noted that the copper acetylides formed under these conditions are less explosive and more stable than those known hitherto. Thorough removal of acetylenic hydrocarbons from hydrocarbon fractions containing butadiene or isoprene is achieved by rapidly passing the gaseous mixtures at 50° to 100°C through a suspension of metallic sodium in xylene[90-92]. The acetylenic hydrocarbons are then completely extracted: acetylene is bound as the acetylide and the higher acetylenic hydrocarbons are polymerised.

Procedures have been described[93-95] for the removal of acetylene from gaseous mixtures containing it in amounts of 14–29 vol. % by passing them through a suspension of VB or VIB metal halides or complexes in aliphatic or naphthene hydrocarbons. The degree of extraction of acetylene is 76–96%. A method for the elimination of acetylene from crude ethylene by treating a stream of ethylene with an aqueous solution of a mercury(II) salt in the presence of oxygen and iron(III) ions has been patented[96]. Such treatment for 1 h results in a decrease of the concentration of acetylene in ethylene from 0.67 to 0.003 vol. %.

Chemisorption by solids is used to eliminate acetylenic hydrocarbons from gas streams, for example from ethylene. Zeolites based on silver[97] and also silver halides and copper(I) and mercury(I) halides or oxides dispersed on porous carriers (alumina gel, silica gel, etc.) have been proposed as sorbents[98,99]. A high efficiency of purification is achieved only when the amount of the acetylenic hydrocarbon impurity in the streams undergoing purification is very low. For example, when the process is carried out using a type X zeolite containing about 35 wt. % of silver at 65°C and a space velocity of 18 000 h^{-1}, ethylene containing 2×10^{-5} vol. % of acetylene is obtained when the initial acetylene concentration is 6×10^{-4} vol. %.

The sorption methods for the removal of acetylenic hydrocarbon impurities are frequently employed on a semi-industrial or industrial scale[32,34,36-39,41,42,57-61,67-71,73,86]. However, in most cases[32,34,44,53,62,63,77,83,84] they do not reduce the acetylenic hydrocarbon content in the mixtures purified to the required limit. For many hydrocarbon systems the selectivity of the sorption method is low, as a result of which a considerable amount of the main products (up to 10%) is lost together with the acetylenic hydrocarbons removed. The industrial employment of the chemisorption procedures involves serious difficulties. The process becomes explosive, since explosive copper acetylides are always formed[100]. The spent solutions are not satisfactorily regenerated[101], which leads to a non-productive consumption of copper salts. Therefore the chemisorption method is largely used in analytical chemistry for the detection and quantitative determination of very low

concentrations of acetylenic hydrocarbons, in particular acetylene, in gaseous mixtures[102-120]. Moreover, the sorption procedures for the removal of acetylenic hydrocarbons involve a considerable consumption of reagents, are complicated, and laborious. Nevertheless, in large-scale manufactures, the absorption of acetylenic hydrocarbons by selective solvents at a low temperature under high pressure is an effective method for the preliminary separation of comparatively large amounts of acetylenic hydrocarbons present in various hydrocarbon systems. The subsequent additional thorough elimination of small amounts of acetylenic hydrocarbons can be achieved by other methods.

2. DISTILLATION

The distillation methods are most suitable for the separation of complex hydrocarbon mixtures into individual fractions in terms of the number of carbon atoms. The isolation of individual components from these fractions and even more so the removal of acetylenic hydrocarbons with the same number of carbon atoms involve considerable difficulties and require clear-cut fractionation. Nevertheless the method of low-temperature fractionation is used in some cases to remove acetylenic hydrocarbon impurities from hydrocarbon mixtures.

Procedures have been proposed for the preparation of pure vinyl chloride by fractionating the acetylene hydrochlorination products[121-123] or the products of the interaction of acetylene with 1,2-dichloroethane[124]. The yield of vinyl chloride containing 0.005 mole % and less of acetylene amounted to about 90% on a column equivalent to 30 theoretical plates (t.p.) with a reflux number of 10.

The possibility of the preparation of specially pure vinyl chloride by a fractionation method has been investigated and it has been shown[125] that, in a column with the same efficiency as above but with a reflux number of 23, it is possible to isolate about 90% of vinyl chloride containing less than 0.001 mole % of acetylene and other impurities, except methylacetylene. The removal of the latter requires a column equivalent to more than 60 theoretical plates. Other investigators[126] obtained by this method vinyl chloride containing 5.5×10^{-7} mole % of acetylene.

When the boiling point of the acetylenic hydrocarbons and the main substances are very close, for example in the case of diolefins and higher acetylenic hydrocarbons or vinyl fluoride and acetylene, the usual fractionation method is relatively ineffective and leads to the loss of considerable amounts of the products purified. In such cases extractive[127,128] or azeotropic fractionation[129-133] is employed. A gaseous mixture comprising vinyl fluoride and 1,1-difluoroethane is freed from the acetylene impurity by azeotropic fractionation with ethane, which forms with acetylene an azeotrope boiling at −94.5°C. The product specimens obtained contained 1−5 vol. % of ethane and 0−2 vol. % of acetylene[129,130]. Azeotropic fractionation of mixtures containing butadiene with an admixture of isobutane[131,132] resulted in a decrease of the concentration of vinylacetylene from 0.49 to 0.08 wt. %.[122] It has been suggested that rectified isoprene be freed from the acetylenic hydrocarbon impurity by azeotropic fractionation in the presence of isopentane and maleic anhydride[133]. Columns equivalent to 60−90 theoretical plates are normally employed. With a reflux number of 50, the acetylenic hydrocarbon content in the mixture becomes only several times smaller.

The distillation methods for the removal of acetylenic hydrocarbons are widely used in the industrial manufacture of vinyl chloride and butadiene. The purification processes are carried out on high-efficiency columns with high reflux numbers. Nevertheless they do not ensure a high degree of purification[134] and result in a loss of up to 10% of the desired product even when the difference between the boiling points of the components is considerable[123,125]. A clear-cut low-temperature fractionation is restricted by the risk of explosion of acetylenic hydrocarbons in the liquid and solid states and in the gaseous state under pressure. The extractive and azeotropic fractionation procedures somewhat alleviate the above difficulties but here too the desired products are frequently contaminated by additional impurities[129,130]. Therefore the distillation method can be employed successfully for the preliminary elimination of acetylenic hydrocarbons in the purification of various products with subsequent additional fine purification by more effective methods, for example by hydrogenation[135].

3. CATALYTIC HYDROGENATION

The first studies on the selective hydrogenation of acetylenic hydrocarbons in the presence of olefins were carried out in the USSR.[136,137] It proved possible to reduce even very small amounts of acetylenic hydrocarbons to ethylenic derivatives in the presence of a large excess of the latter. It was shown that the process selectivity depends on the catalysts employed and the hydrogenation conditions.

Palladium dispersed on various carriers (alumina gel, silica gel, activated charcoal, glass, etc.) is widely used as a catalyst for the removal by selective hydrogenation of the admixture of acetylenic hydrocarbons from concentrated olefinic fractions (C_2 and C_3),[11,138-157] butadiene[158-161], coking gas[162-166], and vinyl fluoride[167]. The hydrogenation is usually carried out in the gas phase at 100−320°C, 5−50 atm, and a space velocity up to 20 000 h^{-1} using catalysts containing 0.001−0.1 wt. % Pd. In many cases[143,148,160,166] the amount of acetylenic hydrocarbons in the streams undergoing purification diminishes from 0.8 to $(1-5) \times 10^{-4}$ vol. %. In order to enhance the initial selectivity, the catalyst is first treated with hydrogen at a working pressure and a temperature higher by 30 deg than the working temperature[168,169]. Frequently, in order to ensure a high selectivity of the catalyst in the hydrogenation of acetylenic hydrocarbons, it is promoted with copper, silver, iron[170-175], chromium[176,177], lithium[161,178], ruthenium, and rhodium[179,180], the process is carried out in the presence of water vapour[181], and the mixture undergoing purification is inhibited with alkyl sulphides[182], halogeno-derivatives of aromatic hydrocarbons[183], or cyclohexane derivatives[184].

Catalysts containing platinum are used to eliminate acetylene from ethylene mixtures[185] and coking[186,187] and other industrial gases[188] at an elevated temperature and pressure. The concentration of acetylene in the purified streams is 2×10^{-4} vol. % and less. Methods have been patented in which concentrated C_2 and C_3 fractions are freed from acetylenic hydrocarbons by liquid-phase hydrogenation between −40° and +50°C and at pressures between 12 and 36 atm on palladium, platinum, or mixed nickel−thorium catalysts[189-191]. The content of acetylenic hydrocarbons then falls from 0.7 to 0.002%.

Apart from platinum subgroup metals, other metals and their compounds are also employed as catalysts for the

selective hydrogenation of acetylenic hydrocarbons. In particular, nickel on kieselguhr is used for the liquid-phase hydrogenation of acetylenic hydrocarbons in the butene–butadiene fraction of the gases obtained in the pyrolysis of petroleum products[192,193], in the dehydrogenation products of isopentane and isopentenes, or in concentrated isoprene[194,195]. As a result, acetylenic hydrocarbons are removed to the extent of approximately 75–95%. The elimination of small amounts of acetylenic hydrocarbons from olefins and diolefins is achieved by hydrogenation over catalysts consisting of reduced nickel[196-201], a mixture of nickel[202,203] or cobalt[204] oxides and sulphides, and nickel or cobalt[205] phosphides on a porous carrier. The process is carried out at 20–315° and pressures up to 70 atm; it yields a product containing less than 1×10^{-4} vol. % of acetylenic hydrocarbons. When ethylene containing 7.6 vol. % of acetylene is passed through a catalytic solution of a nickel cyanide complex at 0–60°C, the effluent gas contains only 0.2 vol. % of acetylene[206]. Mixed nickel–chromium catalysts on carriers are used in the purification of cracking gases[207] and in the gases produced in the pyrolysis[208,209] of a hydrocarbon raw material and in the ethylene fraction of coking gas[210] and the crude ethylene–propene fraction[211]. Selective hydrogenation is carried out at 100–400°C, pressures up to 30 atm, and a space velocity in the range 300–6000 h^{-1}. As a result, virtually complete elimination of acetylenic hydrocarbons from the mixtures is achieved. Catalysts consisting of mixtures of the oxides of cobalt and molybdenum[212,213], nickel and molybdenum[214], and cobalt, nickel, and molybdenum or chromium[215-218] or the sulphides of cobalt, nickel, and molybdenum[219,220] on alumina proved to be effective and selective catalysts. In order to improve the selectivity of the hydrogenation process and to increase the useful life of the catalyst, acetylenic hydrocarbons are removed in the presence of water vapour or sulphur compounds[216]. The above catalysts ensure the elimination of acetylenic hydrocarbons from olefins and diolefins to the extent of 92–100%. Iron–chromium and copper–chromium catalysts promoted with alkali and alkaline earth metal compounds are used to eliminate acetylenic hydrocarbons from olefinic and diolefinic hydrocarbons[221-231] and the gases produced in the processing of mazut[232] at 30–370°C, a pressure up to 70 atm, and a space velocity in the range 200–1000 h^{-1}. The purified products contain about 3×10^{-4} vol. % of acetylenic hydrocarbons, while their initial concentration was 0.16 vol. %. It has been noted that iron–chromium catalysts[221-224,232] give rise to a prolonged induction period in the course of which the products underoing purification are consumed. The purification of converter gas on a zinc–chromium–copper catalyst[233], of pyrolysis gases on an aluminium–chromium–nickel catalyst[234], and of ethylene on a copper–chromium–manganese catalyst[235] has been investigated. In many cases these catalysts ensure virtually complete removal of acetylenic hydrocarbons and have considerable advantages over other catalysts tested, for example those containing palladium, platinum, iron, etc. The effective elimination of acetylene from coking gas[236,237] and concentrated olefins[238] is achieved by its selective hydrogenation on silver catalysts at 150–400°C, 11–15 am, and a space velocity of 3000–4000 h^{-1}. The concentration of acetylene in the gases after purification is 0.0003–0.008 vol. % for an initial concentration of 0.15–0.8 vol. %. The acetylenic hydrocarbon impurity is removed from olefins and diolefins by hydrogenation at 38–315°C, pressures up to 70 atm, and a space velocity in the range 100–2500 h^{-1} using copper catalysts[239,240], sometimes promoted with zinc[241] or Group VIII metals[242]. For example, acetylene is hydrogenated to the extent of 97% on a copper–zeolite catalysts[240], the yield of ethylene being 60% and of ethane 40%. Processes for the removal of acetylenic hydrocarbons from butadiene on an iron powder catalyst at somewhat elevated temperatures and pressures[243], from coking gas on a boron oxide catalyst at 300°C, 50 atm, and a space velocity of 2000–10 000 h^{-1},[244] and from olefin-containing mixtures by bringing them into contact with a palladium–molybdenum catalyst at 200–430°C[245] have been described. Three catalysts (their composition has not been published) for the selective hydrogenation of acetylene in gases from the thermal cracking of ethane, propane, and heavy hydrocarbons have been investigated[246]. The catalysts were tested at 177–316°C, 3–10 atm, and a space velocity of 500 h^{-1}. The concentration of residual acetylene in the purified gases did not exceed 1×10^{-4} vol. %.

The method of selective catalytic hydrogenation has been recognised as the most economical among the existing procedures for the removal of acetylenic hydrocarbons from hydrocarbon mixtures[247,248]. It is widely used in industry[11,144,164,166,181,193,208,218,233,246-252] and in most cases ensures the required degree of purification. However, the hydrogenation method frequently requires the use of expensive palladium and platinum catalysts, which are the most selective[253] but are also very sensitive to other impurities[254] and are difficult to regenerate[255,256]. Moreover, in the purification process the desired products are hydrogenated together with the acetylenic hydrocarbons[193-195,200,208,250,257]. The activity of the catalyst employed is particularly high in relation to the hydrogenation of conjugated bonds in diolefins[192,193,195,256,258] and therefore the losses of the latter in purification are considerable, reaching 8–20%.[145,161,193] As a result it proved possible to achieve the simultaneous elimination of acetylenic hydrocarbons and diolefins from mixtures with a high olefin content[149,176,189-191,209,234,259]. In the case of acetylenic hydrocarbons which also contain a double bond, the hydrogenation of the triple bond is not selective[258,260,261]. Many hydrogenation catalysts have a very prolonged (up to several days) induction period during which the desired products are consumed[222-224] and some of them lose their initial selectivity during operation[262] and lead to the occurrence of side reactions with formation of a wide variety of substances[263-265]. Therefore studies are being made in order to find and develop new catalysts and hydrogenation methods. In particular, in the elimination of acetylenic hydrocarbons hydrogenation is combined with a preliminary application of other methods, for example fractionation, in order to reduce the losses of the main products[135,266].

4. CATALYTIC OXIDATION

Thermal oxidation of acetylene requires the use of relatively high temperatures and leads to a complex composition of the reaction products[297]. When the process is carried out in the presence of catalysts[268,269], it is possible to reduce the reaction temperature appreciably and to obtain only carbon dioxide and water as the final oxidation products.

The catalytic oxidation method is most widely used in the removal of acetylene from air in the manufacture of oxygen[9,270-276]. It has proved possible to oxidise acetylene on catalysts at the temperature to which air is heated in compressors for the collection and compression of air (at about 150°C). Catalysts based on silver[9,271,273-276],

manganese[9,270-273], copper[9,270,271,273], palladium, and rhodium[277-279] are the most effective in the oxidation of small amounts of acetylene in air. Manganese ore promoted with silver[280], MnO_2, or Hopcalite[281] are used under industrial conditions. The purification processes are usually carried out at space velocities up to 60 000 h^{-1} and pressures up to 7 atm. After purification the acetylene content in air is 1×10^{-6} vol. % and less.

The method of selective catalytic oxidation is also used for the removal of small amounts of acetylene from certain hydrocarbon mixtures. It has been suggested that gas mixtures with a high ethylene and butadiene content and also hydrocarbon and petroleum cracking gases be freed from an admixture of acetylene using as catalysts metallic copper or CuO on carriers[282-286]. The process is carried out at a temperature of 120–375°C, a space velocity of 100–300 h^{-1}, and in the presence of a 25% excess of oxygen. The purified mixtures virtually do not contain acetylene. However, since the excess oxygen is always consumed in the oxidation of other hydrocarbons, considerable losses of the desired products are observed. In order to improve the selectivity of the purification process, it is recommended that platinum subgroup metals be employed as oxidation catalysts[287-290] and that acetylene be removed with the aid of catalytic solutions or the gas stream be saturated with water vapour. The purification is carried out at 20–300°C and 1–3 atm in the presence of variable-valence metal salts ($CuCl_2$, $FeCl_3$, etc.).

Thus the method of elimination of the acetylene impurity from hydrocarbon systems by its oxidation to carbon dioxide and water requires the employment of expensive catalysts, in particular those based on silver and platinum and also an excess of oxygen, which makes the process liable to risk of explosion and gives rise to considerable losses of the main substance as a result of oxidation.

5. CATALYTIC POLYMERISATION

Several extensive reviews have been published on the condensation and polymerisation reactions of acetylene and its derivatives[26,291,292]. For the purpose under discussion, catalytic methods of polymerising acetylenic hydrocarbons are of interest, since they make it possible to achieve a high degree of process selectivity and high conversions of the acetylenic hydrocarbons. Copper and its compounds have the most intense polymerising effect of acetylenic hydrocarbons.

Recently attempts have been made to employ the capacity of acetylenic hydrocarbons for rapid and easy polymerisation in the elimination of such impurities from various gaseous mixtures. Several procedures for the removal of the acetylenic hydrocarbon impurity from the liquid C_3 fraction[293], the ethane–ethylene fraction[294], olefins[295,296], and products of the oxidative pyrolysis of methane[297] with the aid of aqueous solutions of univalent and bivalent copper have been described. At 60–100°C and in some cases under a high pressure, acetylenic hydrocarbons are converted into liquid and solid polymers, which are separated from the catalytic solution by distillation and filtration. The degree of extraction of the acetylenic hydrocarbons depends markedly on the rate at which the mixture to be purified is passed through the catalytic solution and amounts to not more than 99.6–99.7%. This entails the formation of explosive copper acetylides. In order to improve the process selectivity, it is recommended that acetylenic hydrocarbon be eliminated[294,295] in the presence of oxidants (O_2, air, copper oxides, etc.) capable of maintaining the pH of the solution in the range 1–4.5.

More far-reaching polymerisation of acetylenic hydrocarbons with formation of solid polymers is also employed for the selective removal of the acetylenic hydrocarbon admixture from various hydrocarbon mixtures. In this case the polymerisation products are deposited on the surface of the catalysts and are periodically removed by burning off with an oxygen-containing gas when the catalysts are regenerated. Methods have been patented for the removal of acetylenic hydrocarbons from butadiene[298,299], halogenated olefins[300,302], olefins[299,302-305], and a mixture of olefins and diolefins[306]. The purification processes are usually performed in the gas phase in the temperature range 0–500°C at atmospheric or elevated temperature (up to 35 atm) and a space velocity in the range 500–2500 h^{-1}. Copper and its oxides[298-301,304,305], $CuAl_2O_4$,[302] a catalyst for the cracking of hydrocarbons, for example the aluminosilicate catalyst, deactivated with an alkali metal oxide[303], crystalline zeolites with pore diameters of 6–15 Å and containing between 0.5–12 wt. % of the metal promoting the acetylenic hydrocarbon polymerisation reaction (copper, nickel, cobalt, silver, etc.),[306] and a copper–aluminium alloy with an activated surface[307] are employed as catalysts. As a result of purification, the acetylenic hydrocarbon content decreases in most cases to $(1-5) \times 10^{-4}$ vol. %. It has been stated[298,308] that there are considerable losses (up to 7–12%) of the substances purified in consequence of polymerisation and other reactions on catalysts.

The advantages of the above methods of purification are as follows: elimination of the risk of explosion in the process[300-302,307]; the attainment of exceptionally high selectivity of the catalysts in relation to the polymerisation of acetylenic hydrocarbons to solid polymers[301,302,307]; high efficiency of the elimination of acetylenic hydrocarbons over a wide range of the process parameters and acetylenic hydrocarbon contents in the mixtures purified; ease of regeneration of the catalysts[298-302,304,305,307,308], etc. Therefore, it appears that the method of elimination of acetylenic hydrocarbons from hydrocarbon systems by selective polymerisation to solid polymers is the most convenient, compared with other procedures available, is technologically simplest, and comparatively cheap. It is very promising for the removal of small amounts of acetylenic hydrocarbons from various mixtures, i.e. for a high degree of purification. This is why this method of purification is of considerable practical interest for the large-scale manufacture of monomeric olefins, their halogeno-derivatives, diolefins, and other products, from which very small amounts of acetylenic hydrocarbons must be carefully removed. It is significant that this method is used for the additional purification of the stream of product after the removal of acetylene by selective catalytic hydrogenation.

The present author[309] made for the first time a systematic study of the fair elimination of acetylenic hydrocarbon impurities from hydrocarbon mixtures by the polymerisation method. The catalyst based on the copper spinel of aluminium was recognised as the most effective and promising[302,310]. Therefore all the principal characteristics of the purification and regeneration process were investigated on this catalyst[310,311]. In particular, it was shown that the spinel catalyst has a high mechanical strength and is most promising for continuous purification processes with a stationary bed[311]. A design calculation was made as an example for an industrial purification reactor and the optimum process conditions were selected[312].

6. OTHER METHODS

Apart from the methods discussed, other methods have been proposed for the removal of acetylenic hydrocarbons from various gas mixtures, among which the following may be mentioned.

In order to eliminate 0.1–1.0 vol. % of acetylenic hydrocarbons from a gas, it is mixed with SO_2 to give the proportions SO_2 : acetylenic hydrocarbon = (0.6–2.3) : 1. The resulting mixture is brought into contact at a temperature between −18° and 93°C, a pressure of 0.1–0.4 atm, and a space velocity of 200–1500 h^{-1} with a catalyst consisting of $AgNO_3$ on an inert porous carrier[313].

It is recommended that acetylenic hydrocarbons be removed from vinyl fluoride[314,315], the C_2 fraction[316], and propene[317] by selective hydrochlorination at 100–150°C in the presence of catalysts, for example $HgCl_2$ on activated charcoal. The resulting chloro-derivatives of acetylenic hydrocarbons are readily removed from the mixtures purified by the distillation method. As a result of purification, the acetylenic hydrocarbon content decreases, for example from 1.48 to 0.051 vol. %.

Methods have been described for the removal of acetylenic hydrocarbon impurities from hydrocarbon gases, in particular pyrolytic gas, by amination[318–320]. This method of purification is based on the fact that at an elevated temperature and in the presence of catalysts acetylenic hydrocarbons react with ammonia to form heterocyclic compounds (picolines)[321]. The purification is carried out at 170–400°C using zinc and molybdenum oxides[318,319] or copper(I) chloride[320], all deposited on activated Al_2O_3, as catalysts. For example at 350°C, atmospheric pressure, and a space velocity of 50 h^{-1} in the presence of 10 wt. % NH_3, the content of acetylene in pyrolytic gas decreases from 0.25 to 0.001 vol. %. The ethylenic hydrocarbons present in pyrolytic gas remain unchanged.

The concentration of acetylenic hydrocarbons in the C_4 pyrolytic fraction decreases from 0.03 to 0.007 vol. % when it is passed over an oxide catalyst (Al_2O_3, SiO_2, MgO, or their mixture) with an effective acidity of 1.5–8 at 27 to 120°C.[322] The catalyst must be subjected to a preliminary heat treatment at 480–650°C for 1–24 h.

In order to remove the acetylene impurity from vinyl fluoride[323], the gas mixture is treated with a solution of mercury salts in 10–50% H_2SO_4. Acetylenic hydrocarbons are removed similarly from diolefins[324]. It has also been recommended that mixtures of vinyl fluoride, acetylene, and 1,1-difluoroethane be brominated at 0°C with subsequent distillation of the bromination products[325]. Pure vinyl fluoride is obtained in a yield of about 80% by the debromination of 1,2-dibromo-1-fluoroethane with zinc dust in an alcoholic medium.

IV. ANALYTICAL METHODS FOR THE DETERMINATION OF ACETYLENIC HYDROCARBON IMPURITIES IN VARIOUS MIXTURES

A necessary condition for the further improvement of the methods for the thorough elimination of acetylenic hydrocarbons from various systems is the development of highly sensitive analytical control procedures at the right time. They should make it possible to determine with adequate accuracy the composition of a wide variety of complex mixtures, to estimate quantitatively small amounts of acetylenic hydrocarbon impurities in the mixture, to carry out rapidly large-scale analyses, to achieve a continuous analytical control of the operation of industrial apparatus, and to regulate automatically the course and conditions of technological purification processes. Nowadays various methods are used for this purpose: chemical, physicochemical, and physical.

The characteristic red colour of copper acetylide, obtained in ammonia solutions of copper(I) salts, is used for a qualitative detection of traces of acetylene in various mixtures[102,103,310]. Test papers[104] and also a microchemical method for the determination of acetylene[105] have been developed on this principle. In order to maintain a stable colour of the precipitate for a long time and to increase the sensitivity of the reaction, it is recommended that reducing agents and gelatine be added to the solution. The sensitivity of the freshly prepared reagent with respect to acetylene is 2×10^{-4} vol. %. A method developed for the semiquantitative determination of acetylene in gas mixtures[326] depends on the fact that in the presence of acetylene the yellow colour of the reagent [silica gel impregnated with a mixture of $PdSO_4$ and $(NH_4)_2MoO_4$] becomes yellow-green. The sensitivity of the reagent is 10^{-3} vol. %. Sometimes acetylene is detected in mixtures using the formation of a protective layer on Ag_2CrO_4.[327] When acetylene reacts with Ag_2CrO_4 solution in nitric acid or ammonia, a flakey orange or yellow precipitate is formed. The minimum amount detectable is 1 μg of acetylene.

Among the chemical and physicochemical analytical methods for the quantitative determination of small amounts of acetylenic hydrocarbons, the commonest are absorption, titrimetric, colorimetric, and other methods. The best reagent for the determination of acetylene in hydrocarbon gas mixtures by the volumetric absorption method is an alkaline solution of potassium iodomercurate[328–332]. It has been shown that small amounts of acetylene in oxygen and in air[333] and also in other gases[334] may be determined volumetrically using solutions of copper and silver salts. The acetylene content in concentrated vinyl fluoride has been determined by absorption in bromine water[130]. It is noteworthy that the volumetric method is usually applicable when the content of the acetylenic hydrocarbon is high, i.e. is not less than 0.5%. In this case the error of the determination is ±0.2 abs. %. The use of special apparatus makes it possible to determine from the change in volume even lower concentrations of acetylenic hydrocarbons in the mixture. However the error of the determination then increases appreciably, since the absorption solutions containing copper, silver, and mercury also absorb a certain amount of other components of the mixture analysed (olefins, diolefins, carbon monoxide, molecular oxygen, etc.).

The alkalimetric titration method[335], which depends on the interaction of acetylene and its monosubstituted derivatives with $AgNO_3$ solution followed by titration of the liberated nitric acid with alkali in the presence of a mixed indicator (an alcoholic solution of Methyl Red and Methyl Blue) has been widely adopted in analytical practice for the determination of the overall content of acetylenic hydrocarbons. It is used to determine the admixtures of acetylenic hydrocarbons in ethylene[335], butadiene[14,102], isoprene[336,337], nitrogen and air[338], and also in other mixtures[339–341]. A combined method for the separate determination of acetylene and higher acetylenic hydrocarbons has been described[342,343]. The amount of acetylene is calculated from the weight of the readily crystallisable complex $C_2Ag_2.AgNO_3$ formed when acetylene reacts with a concentrated solution of $AgNO_3$. Higher acetylenes do not form a precipitate. Therefore the overall content

of acetylenic hydrocarbons is found by alkalimetric titration and the content of higher acetylenes is obtained by difference. A method for the determination of small amounts of acetylenic hydrocarbons in gases[103], based on their interaction with an ammoniacal solution of $AgNO_3$ and subsequent titration of the excess $AgNO_3$ with NH_4SCN, has been recommended. Titrimetric methods make it possible to determine the contents of acetylenic hydrocarbons in mixtures to within 5 rel. % with a sensitivity of 10^{-4}%.

Small amounts of acetylene in various gas mixtures are determined successfully with a high accuracy by a colorimetric method[107-111] based on the interaction of acetylene with copper(I) salts in ammoniacal solution. The finely dispersed copper acetylide colours the solution red-violet. Acetylene is determined by colorimetric measurements on the solution against a standard scale[107,108,112-116]. Special apparatus has been designed and methods for the colorimetric determination of acetylene has been improved[117-119]. In some cases[120], in the determination of small amounts of acetylene in air it is sorbed on silica gel at −78°C and the sorbent is then treated with a mixture of an ammoniacal solution of $CuCl_2$ and a solution of $NH_2OH.HCl$. The colour of the silica gel is compared with a standard scale. For this purpose, a linear colour method of determining acetylene in air has been developed[344,345]: air is passed through an indicator tube filled with coarsely porous ShKS silica gel impregnated with potassium iodide; a pale-brown layer is formed in the indicator powder, whose length is proportional to the concentration of acetylene in air. The sensitivity of colorimetric analytical methods is 1×10^{-4}% and the accuracy of the determination is not more than to within 0.05 abs. %.

A polarographic method is used to determine dissolved acetylene[346,347] or its admixtures in gaseous products, for example in chloro-derivatives of ethylene[348,349].

Among physical methods for the analytical determination of acetylenic hydrocarbons in various mixtures and specially pure compounds, gas–liquid partition chromatography has been widely and successfully used. Chromatographic analytical methods have significant advantages over other procedures, namely they are universal, i.e. they yield information about a number of impurities, are very sensitive, rapid, and accurate, it is possible to work with very small samples of materials, the analysis can be automated, etc. Therefore they are the most promising. Numerous studies on the chromatographic analysis of specific systems containing acetylenic hydrocarbon microimpurities are being systematically published in the periodical literature on science and engineering. Ethylene[350-358], propene[359,360], isobutene and butadiene[14], vinyl fluoride[361,362], vinyl chloride[363-366], pyrolysis gases and the ethylene fraction[367-369], coking gas[370], and other products[371-373] have been analysed by gas–liquid partition chromatography. In most cases apparatus with flame-ionisation or argon detectors is employed. A wide variety of adsorbent, depending on the nature of the products analysed, are used as packing for chromatographic columns. The sensitivity of chromatographic analytical methods with respect to acetylenic hydrocarbons is 10^{-3}–10^{-7}%, the accuracy of the determination being to within (5–20) rel. %.

Among other physical methods for the analytical determination of acetylenic hydrocarbon impurities, which do not require the separation of the initial mixtures into components, certain spectroscopic procedures are employed. Infrared spectroscopic data are used to determine the purity of ethylene and the content of acetylenic hydrocarbons in ethylene[374,375], vinyl fluoride[376], and other mixtures[377-379]. Certain improved analytical techniques have been proposed[380]. The sensitivity of the method is 4×10^{-3} vol. % and the accuracy of the determination is to within 10 rel. %. Attempts have been made to employ the mass-spectrometric method for the analysis of certain mixtures, for example coking gas[381] and the gases in the synthesis of vinyl fluoride[382] in order to determine the acetylenic hydrocarbon impurity. However, isomeric hydrocarbons and compounds with the same number of carbon atoms in the molecule are difficult to determine by the mass-spectrometric procedure. In the analysis of complex mixtures, the sensitivity and accuracy of this method are greatly impaired. A combination of the gas–liquid chromatographic and mass-spectrometric methods appears promising[383].

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