



# **Alvigo Group of Companies. Technologies**

## Ammonia Production



The nitrogen industry, the largest in the world and advanced as for technical solutions, was created over the years of GIAP existence based on developments achieved by its research workers and engineers. About 70 ammonia plants with a capacity ranging from 55000 to 450000 tpy were designed and constructed. A unique Togliatti-Odessa ammonia pipeline was built allowing to export liquid ammonia to many regions of the world. The designs developed by the Institute were used to build nitrogen industry facilities in Afghanistan, Bulgaria, Germany, China, Cuba, Romania.

### NEW PROCESS TECHNOLOGIES FOR AMMONIA PRODUCTION

As for this line of activities at present the company carries out technological developments and develops the designs to:

- revamp the operating ammonia plants
- transform surplus ammonia plants into methanol plants
- create integrated ammonia-methanol, ammonia-hydrogen, etc. plants
- develop ammonia plants based on the state-of-the-art technology achievements to replace the operating ones.

To perform the above activities the company has expertise and experience practically for all process stages of ammonia, methanol, hydrogen, etc. plants. The specialists of the company participated in the development of the process and equipment for many large-scale chemical plants as well as in their startup. In 1998 an ammonia plant was designed and put into operation in China with their participation using the most modern energy-saving technology being above the world standards. At present advanced ammonia production technologies with specific energy consumption of 6.64 Gcal per ton of NH<sub>3</sub> are developed. For modernization of the plants, technical solutions to increase the capacity of large-scale ammonia plants to 1800 tons per day, designs to revamp ammonia and methanol converters, high temperature and low temperature shift converters, mixers for reformers, etc. are developed.

### GIAP's Ammonia Technology with Low Energy Consumption

When developing the concept of a new ammonia plant we considered the following aspects of the problem:

**Thermodynamic aspect.** First of all it is necessary to reduce steam production by limiting to unavoidable process needs, and generation of mechanical energy used for compression of process streams as well as hydraulic losses. In this case unavoidable heat recovery should be carried out at the highest temperature level.

**Ecological aspect.** It may be assumed that limitations as for the used primary fuel and steam production would tell on the amount of liquid and gaseous effluents into the environment. We proceeded from the need to reduce the hazardous gas emissions by a factor of three-four and practically completely eliminate process condensate effluents.

**Reliability and safety.** It should be taken into consideration that reliability and safety of the plant enhance if you succeed to reduce the portion of equipment operating at the highest temperature and pressure, simplify the compressor, eliminate high pressure steam lines and turbines where HP steam is used. The control system should ensure reliable operation of all units comprising the plant, have subsystems for equipment condition diagnosis, process and display their data.

**Technical solutions.** Thermodynamic considerations on which the energy saving concept is based are realized by using the latest GIAP's developments in the field of process technology, equipment and catalysts.

### Basic energy consumption figures for ammonia plant based on the GIAP's technology.

The below Table gives energy consumption figures per ton of ammonia for the ammonia plant operating at synthesis pressure of 80 bar where the lowest mechanical energy generation is achieved – about 0.566 MW per ton of ammonia.

Table 1

#### BASIC RAW MATERIAL, ENERGY AND MATERIALS CONSUMPTION FOR AMMONIA PLANTS USING GIAP'S TECHNOLOGY

per 1 ton of NH <sub>3</sub>	
Synthesis cycle pressure, bar	80
Natural gas, m <sup>3</sup> heating value of 8807 cal/m <sup>3</sup>	708.1
Oxygen, m <sup>3</sup>	0
Electric power, kWh	481.5
Boiler feed water, m <sup>3</sup>	0.73
Cooling water, m <sup>3</sup>	80.6
Total energy consumption, GJ	28.01

### Software for process engineering solutions

Software for chemical process modeling is of great importance for development of state-of-the art technologies. GIAP has developed software to compute processes that run in catalytic reactors as the ammonia production is based greatly on catalytic processes and its further development is associated with the progress achieved in the heterogeneous catalysis research field.

One of our developments is the software to compute steam reforming of natural gas using two-dimensional model of catalyst bed that makes possible to:

- predict the composition of produced gas at the exit from the reactor containing the catalyst of different forms and sizes;
- determine the reforming capacity;
- determine the degree of catalyst usage and remaining life of the catalyst;
- calculate optimum volume of the catalyst considering the required capacity of the plant and possible catalyst ageing.
- calculate axial and radial distribution of temperatures, concentrations, stream velocities, etc.

## Methanol production

ALVIGO Group incorporates scientific and design structures involved in development and designing of methanol production plants. We are highly experienced in research of methanol process technology, creation of mathematical modeling software, equipment engineering to effectively realize the process.

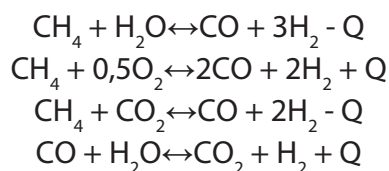
Methanol production plants from 40 thousand/tpy to 1 million/tpy were constructed and successfully operated basing on our designs.

### Short description of process technology

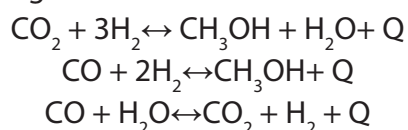
Methanol (methyl alcohol CH<sub>3</sub>OH) is one of the major organic synthesis products and feedstock for production of formaldehyde, acetic acid, dimethyl terephthalate, methyl methacrylate, methyl amine, methyl-tretbutyl amine and other chemical products.

Methanol production process includes synthesis gas preparation, methanol synthesis and distillation stages.

At synthesis gas preparation stage different methods of hydrogen feedstock are used, i.e. vapor, vapor-oxygen, vapor-CO<sub>2</sub>, two-stage reforming. Depending on different oxidizing agents (water vapor, oxygen, carbon dioxide) synthesis gas is produced by the following reactions:



Methanol is produced from synthesis gas:



At distillation stage methanol is separated from water and purified from organic micro-impurities.

Methanol process upgrading consists in bringing to minimum consumption of utilities and development of optimal process equipment implementation.

The first industrial large-scale developments of Alvigo institutes are four 100 thousand/tpy methanol plants (M-100) put into operation during 1975 to 1977 period. The methanol plants were operated using the catalysts developed by Alvigo groups.

### Conventional synthesis in shaft-type reactor

The operating plants have been successfully employed shaft-type methanol synthesis reactors with cold bypasses. During all the time of their operation our specialists have been rendering technical support on plant upgrading, catalyst reduction and bringing the plants to normal operating conditions, production audit, technology and catalyst monitoring.

This integrative approach to the plants constructed by our designs has considerably improved technical

and economic characteristics and made possible to scale up plant capacity to 200 thousand/tpy.

### ***Synthesis in reactor cascade***

Methanol is produced in two or several series-connected cascade reactors operated without gas mixture recycle and producing crude methanol in each reactor. As feedstock various gas mixtures can be used from different sources or obtained by different process technologies, and also waste gases from plants. This technology provides for processing synthesis gas containing CO 1.0 to 33.7 vol.%; CO<sub>2</sub> 0.3 to 22.5 vol.%; nitrogen 0.5 to 50.0 vol.%. High specific catalyst output is attained, i.e. 0.45-2.85 tons of methanol per 1 m<sup>3</sup>/hour at high conversion rate of carbon dioxides to methanol, i.e. 70 to 94 %.

### ***Two-stage methanol synthesis***

Characteristic feature of two-stage methanol synthesis flow diagram is that feed synthesis gas is processed to methanol at 1st stage in tubular flow reactors with intensive removal of reaction heat at high partial pressures of carbon oxides, which considerably increases methanol formation rate. Complete processing of carbon oxides is carried out in recycle reactor at 2nd stage.

The technology ensures significant process intensification due to considerable increase in catalyst specific output and cost reduction for gas mixture circulation.

The technology is defended by certificates of authorship and patents.

### ***Co-production of methanol and other chemical products:***

- methanol and ammonia
- hydrogen and methanol
- methanol and acetic acid
- methanol and DME;

### ***Services:***

Methanol is traditional research area for ALVIGO Group, we are ready for cooperation and can perform the following works:

- Development of technical solutions, basic and detail designs, contract supervision for methanol plants of 10 thousand/tpy to 1 million/tpy based on processing of various feedstock:
  - conversion of natural gas, petroleum, associated petroleum gases;
  - gasification of solid raw materials (coal, biomass, municipal solid waste);
  - effluent gases (coke gas, waste gas of metallurgical plants).
- Methanol plants upgrading and improving technical and economical characteristics, reduction of consumption of power and raw material resources.
- Audit of methanol production plants.

### *Selected references*

Start-up year	Location	Capacity, tpy
tpy	JSC "Schekinoazot", Russia	450 000
2008	JSC "AHEMA", Ionava, Lithuania	130 000
2003	Novomoskovsk branch, CSC "MKhK Evrokhim", Russia	300 000
2003	JSC "Schekinoazot", Russia	140 000, upgrading
2001	JSC "AHEMA", Ionava, Lithuania	74 000
2001	JSC "Metafraks", Gubakha, Russia	750 000, upgrading



## Calcium ammonium nitrate (CAN)

In 2002-2003 the Institute developed and adopted to realization in Public SC "Rivneazot" (Ukraine) a detail design for calcium ammonium nitrate production from ammonium nitrate and natural calcium carbonate, with plant capacity of 400 thousand t/y.

Calcium ammonium nitrate -  $\text{NH}_4\text{NO}_3 : \text{CaCO}_3$ . Ammonium nitrate/ limestone ratio may vary from 60:40 to 80:20, with nitrogen content in the products varying from 21% to 28%, respectively.

Due to calcium carbonate presence physical properties of calcium ammonium nitrate are more favourable compared to ammonium nitrate. In agricultural industry it is used as a complex (nitrogen-calcium-magnesium) granulated fertilizer. Nitrogen in form of nitrate ( $\text{NO}_3$ ) promotes fixation of calcium, which improves color, quality and storability of fruit and vegetables preventing loss in transportation and storage. It is a multi-function fertilizer that can be used for all soil types and agronomic crops. It is widely used in Western Europe countries.

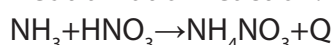
Calcium ammonium nitrate is a neutral fertilizer that enables its transportation to Europe and ensures conformance with requirements on prohibition on transportation of explosive ammonium nitrate within European Union territory.

Calcium ammonium nitrate production process consists of the following units:

- receiving of natural calcium carbonate;
- calcium carbonate silo storage;
- production of ammonium nitrate solution; - mixing of ammonium nitrate solution and calcium carbonate;
- production of finished product;
- bulk storage of calcium ammonium nitrate;
- packing and shipment of finished product.

Ammonium nitrate is produced in neutralization heat utilizing equipment under pressure 0.02 MPa where nitric acid is neutralized by gaseous ammonia of not less than 57% concentration, ammonia and nitric acid having been preheated.

Neutralization reaction:



The heat released during neutralization is used to evaporate a portion of water and produce ammonium nitrate solution of higher concentration. Leaving neutralization heat utilizing equipment ammonium nitrate solution contains 1-5 g/l of free nitric acid, which is successively neutralized by gaseous ammonia in after-neutralizer and, if necessary, in control after-neutralizer (mass concentration of  $\text{NH}_3$  – 0.1g/l). To suppress the reaction of calcium nitrate formation in neutralization heat utilizing equipment the ammonium nitrate solution is treated with sulphuric acid, the latter is also fed to after-neutralizer.

The resulting ammonium nitrate solution of 86-92% concentration is mixed with calcium carbonate and sent to slurry tank wherefrom it is fed to finished product production unit.

Calcium ammonium nitrate slurry is fed to special equipment where moisture evaporation, granulation and drying process to produce calcium ammonium nitrate takes place. Calcium ammonium nitrate is screened on vibration screens.

The finished product CAN is treated with anti-clodding agent and sent to storage.

**The Institute offers to clients the following services:**

Development of design documentation on CAN production process.

Support of design documentation during expert evaluation.

Designer's supervision during construction.



Private SC "Severodonetsk Azot Association"



Ammonium nitrate production plant, JSC "Akron"



## Nitric Acid Production

To the present day nitric acid industry in the former USSR countries remains the largest in the world. It is a basis for production of nitrate nitrogen fertilizers (ammonium nitrate and its modifications) as well as compound fertilizers (containing nitrogen, phosphorus and potassium). The output growth of these fertilizers is inevitable all over the world to solve a food problem. Besides, nitric acid is required for production of explosive agents for peaceful and defense purposes and organic synthesis products.

All existing plants were designed in different years by JSC "GIAP" being a part of Alvigo Group of Companies using proprietary process schemes and based completely on domestic equipment. Most weak nitric acid (58-60% of  $\text{HNO}_3$ ) is produced by UKL-7 plants (single pressure system) and AK-72 plants (dual pressure system). Small-capacity plants based on 1/3.5 atm. dual pressure system are still in operation.

### Special Features of Alvigo's UKL-7 and AK-72 Plants.

The main special feature of these plants is the use of high-temperature power-recovery gas turbines as main drive of air compressor in UKL-7 plant with single 7.3 atm. pressure of air compressor and nitrous gas blower and AK-72 plant with ammonia conversion stage pressure of 4.2 atm. and nitrogen oxides absorption stage pressure of 11 atm.

From thermodynamic point of view the use of high-temperature gas turbines ensures saving of equivalent fuel for nitric acid production not less than 13%. Nitric acid plants with high-temperature gas turbines are most beneficial for natural gas-producing countries and enterprises consuming a lot of steam for other plants.

### Nitric Acid Plant Revamping Activities.

To expand a market of orders for nitric acid plants Alvigo, based on knowledge and engineering experience in this area, focuses on revamping of UKL-7 and AK-72 plants up to partial and even full exclusion of natural gas and development of new plants using imported compressors and blowers.

Today Alvigo performs works on improvement of weak nitric acid plants UKL-7 and AK-72 to increase their capacity, enhance reliability and environmental indices. Alvigo's capabilities allow to design state-of-the-art weak nitric acid plants of various capacities based on various process schemes with due account of Clients' requirements.

### Revamped UKL-7 Plant with New Turbocompressor GTU-8.

Based on Alvigo's technical task to replace worn-out and out-of-date GTT-3M units new GTU-8 unit with much higher technical-and-economic characteristics and operational reliability was designed for air compression.

Revamped UKL-7 plant with GTU-8 unit was designed, commercialized and successfully operated at JSC "Nevinnomyssk Azot".

Process flow diagram with some equipment items was updated. Natural gas consumption was reduced. Plant capacity was increased.

## Technical-and-Economic Characteristics of UKL Plant with New GTU-8 Unit

Air flow to process, Nm <sup>3</sup> /h.....	66 450;
including:	
- air flow to mixer, m <sup>3</sup> /h.....	54 000;
- air flow to stripper, Nm <sup>3</sup> /h .....	7 400;
- air flow to nitrous gas line, Nm <sup>3</sup> /h .....	5 050;
Ammonia flow to mixer, m <sup>3</sup> /h.....	6 550;
Plant capacity, t/h.....	15.7;
Utilities consumption:	
including:	
- electricity, kWh.....	18;
- natural gas, Nm <sup>3</sup> /h.....	1150;
- cooling water, m <sup>3</sup> /t.....	135.2;
- steam output, Gcal/t.....	0.915;
Main process data:	
- conversion degree, %.....	93.5;
- absorption degree, %.....	99;
- conversion temperature, °C.....	890-910;
Main specific consumption figures:	
- electricity, kWh/t.....	1.15;
- natural gas, Nm <sup>3</sup> /t.....	73.2;
- cooling water, m <sup>3</sup> /t.....	135.2;
- steam output, Gcal/t.....	0.915;
Absolute pressure in process system, MPa.....	0.73-0.8.



## AK-72M Plant

AK-72M is modernized AK-72 plant with changing of some systems to increase capacity and remove shortcomings in the process flow diagram and equipment effecting stable operation and technical-and-economic characteristics of the plant which were identified during first years of AK-72 operation.

Main changes:

1. The design plant capacity is increased to 1200-1250 tpd of HNO<sub>3</sub> monohydrate owing to installation of updated machine coded as KMA-2.
2. High-temperature reactor for catalytic treatment over palladium catalyst APK-2 is deleted. Low-temperature catalytic treatment of tail gas over catalyst not containing precious metal AMTS is used.
3. Single-stage tail gas heating to 760°C in high-temperature unit.
4. Heat-exchange surface of WHB economizer and WHB steam output are increased.
5. Cold of liquid ammonia evaporation is used for heat removal at upper cooling trays of absorber, absorption degree is increased.
6. Along with increased plant capacity, modernization gave certain reduction in feedstock, natural gas consumption and increased steam output.

## Acetic Acid Production by Methanol Carbonylation Using Carbon Monoxide at Moderate Pressure.

ALVIGO's experience in the design of acetic acid plants using methanol carbonylation by carbon monoxide is based on the expertise of the specialists employed in the past by State Enterprise "IAP", who were involved in basic engineering of the acetic acid plant for Russia, Iran, China. Khimtekhnologiya as a business unit of ALVIGO carried out some studies for construction of such a plant for JSC Achema (Lithuania), JSC Metafraks (Gubakha, Russia), Iran, etc.

**Acetic acid** is a transparent liquid with a characteristic heavy odour, miscible with many solvents and itself a very good solvent for organic compounds. It can form azeotropic mixtures.

Acetic acid is used in food industry for preparation of marinade, dressings, canned goods, vinegar essence and table vinegar. In pharmaceutical industry it is used for production of medicines such as aspirin, phenacetin.

Acetic acid is used as raw material for production of acetyl chloride, acetic anhydride, dyes, acetates, monochloroacetic acid, insecticides, as solvent for lacquers, rubber latex coagulant, acetylating agent during organic synthesis. Acetates are used for etching during dyeing.

### Description and Purpose of the Product Produced by this Technology

Acetic acid is produced by continuously reacting carbon monoxide and methanol in a mechanically agitated gas-liquid reactor at approximately 185°C and 2.8 MPaG.

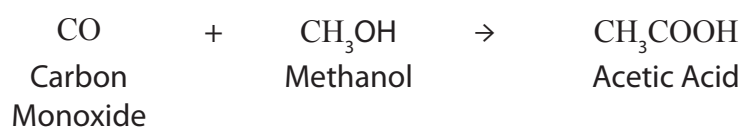
A soluble catalyst system consisting of a rhodium complex (catalyst) and methyl iodide-hydrogen iodide (promoter) causes the reaction to occur at a reasonable rate. The reaction generates heat. Heat of the reaction under synthesis conditions is about 2265 kJ/kg of acetic acid produced.

There are two main reaction systems in the acetic acid process, namely:

- 1) methanol carbonylation by monoxide oxide to form acetic acid ;
- 2) water-gas shift reaction which forms carbon dioxide and water from carbon monoxide and water.

These reaction systems are described below.

1) Carbonylation reaction:



2) Water-gas shift reaction.

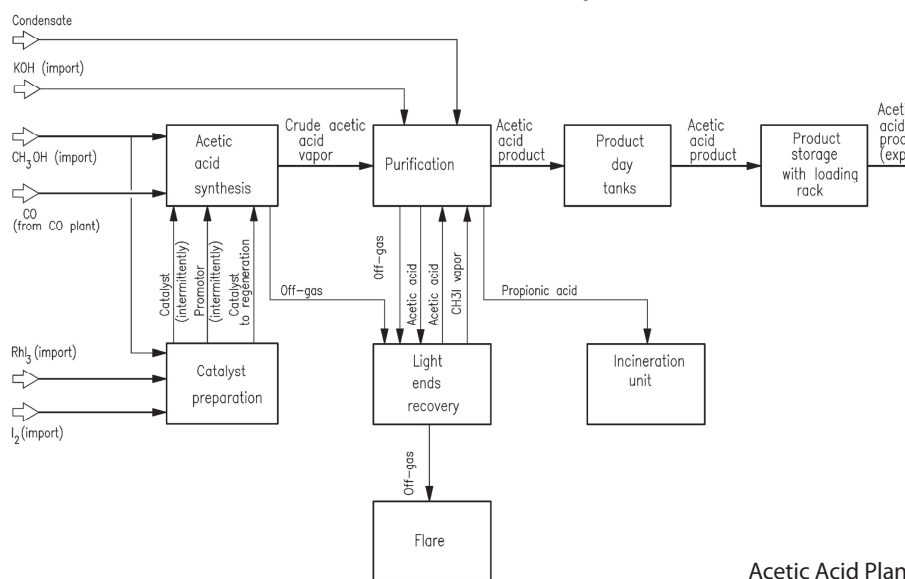
Water-gas shift reaction is the main side reaction:



### Raw Material and Auxiliary Materials Consumption

No.	Raw Material and Materials	Meas. Units	Normal Consumption per 1 Ton	Remarks
1.	Methanol (100%)	kg	567	
2.	Carbon Monoxide (100%)	kg	639	
1.	KOH (100%)	kg	0,068	
2.	Na <sub>2</sub> CO <sub>3</sub> (100%)	g	0,24	
3.	Rhodium Triiodide (as Rh)	g	0,12	
4.	Iodine (100%)	g	120	
5.	Ethylene glycol	g	15	
6.	NaOH (as 42%)	kg	0,5	

Acetic Acid Plant. Block Flow Diagram.



Acetic Acid Plant. Block Flow Diagram.

### Services we can offer for this technology.

ALVIGO can undertake the following scope of activities:

- preparation of investment feasibility study as applied to Customer's conditions (for acetic acid plant proper);
- basic engineering;
- detailed engineering for all project parts including civil engineering;
- placement of orders for equipment manufacture with vendor selection justification in Russia, CIS countries and other countries, preparation of precontract documentation;
- technical support during manufacture;
- designer's supervision during construction, erection;
- participation in startup and performance test.

## Acetylene Production Description and Use of Product Produced Based on Technology

Under normal conditions acetylene ( $\text{CH}\equiv\text{CH}$ ) is a colorless gas highly soluble in many organic and inorganic liquids.

Acetylene is an inflammable explosion-hazardous substance.

Burning releases a lot of heat.

Explosive limits of acetylene-air mixtures depend on mixture temperature and pressure.

Acetylene has a high chemical activity. It is capable of entering into substitution, combination and polymerization reactions, therefore it can be a basis for synthesis of various organic products.

Acetylene is a feedstock for synthesis of monomers used for production of chemical fibers, plastics, rubber and other important products and materials. Such monomers include vinyl chloride, vinyl acetate, acrylonitrile, chloroprene, etc.

Acetylene is used for production of 1,4-butanediol being a basis for manufacturing of polyurethanes, polyesters, effective plastifiers for thermoplastics, gamma-butyrolactone.

Acetylene is used in production of diisocyanates being a feedstock for polyurethane polymers.

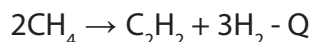
There is acetylene-based production of N vinylpyrrolidone which polymerizes forming polyvinylpyrrolidone used as plasma substitute in medicine.

There are diene synthesis units for production of herbicides for weed destruction in legumes and grain-crops fields.

State-of-the-art technology allows to use acetylene as a feedstock for new production plants.

### Overview of Process, Main Parameters and Consumption Data

Acetylene is formed as a result of oxidative pyrolysis of methane being a main constituent of natural gas by its thermal decomposition at 1400 - 1500°C temperature and atmospheric pressure according to the following reaction:



During methane oxidative pyrolysis the reactions of complete and incomplete methane oxidation, CO shift and partial acetylene decomposition take place along with the reaction to form acetylene. The reaction of acetylene decomposition to carbon and hydrogen produces intermediate products of acetylene thermal condensation forming as a result diacetylene, methyl acetylene, vinyl acetylene and other unsaturated hydrocarbons as well as aromatics such as benzene, etc.

Acetylene constitutes about 8% by vol. in the products of natural gas decomposition and combustion reactions.

Natural gas and oxygen prepurified from mechanical impurities at filters and preheated to 600 - 650°C in fired preheaters are supplied to the reactor mixer. From the mixer methane-oxygen mixture goes to burner and then to reaction chamber where oxidation and thermal decomposition reactions take place. Stabilizing oxygen is admitted to the reactor burner to stabilize the pyrolysis process.

Pyrolysis gas is quenched with cooling water injected into gas stream at the reaction chamber exit.

Injected water quenches hot gas to about 85°C and the reactions are terminated.

Pyrolysis gas is further cooled and purified from carbon black in scrubber and electrical filter.

Pyrolysis gas purified from carbon black leaves the pyrolysis section with 37°C temperature and goes to the pyrolysis gas compression section.

Carbon black water from the reactor, scrubber and electrical filter is sent to the carbon black separation section and then to the local cooling water system.

Steam turbine-driven screw compressor is used for compression. The compressor has two compression stages, interstage gas cooler and aftercooler.

After the second compression stage pyrolysis gas is fed to the concentration section to recover final acetylene product from pyrolysis gas.

Acetylene is recovered from gas mixture by absorption and desorption. N-methylpyrrolidone (NMP) is used as absorbent. Different solubility of pyrolysis gas components allows to fractionate them into 3 main fractions: acetylene, synthesis gas and mixture of higher acetylene homologues.

Hydrogen and carbon monoxide are main components of synthesis gas.

The mixture of pyrolysis gas and circulating gas compressed to 1.18MPa(A) is supplied to the diacetylene absorber. The absorber is refluxed with NMP being diacetylene solvent. In the absorber the solvent absorbs diacetylene and other higher acetylenes.

Diacetylene-free gas is fed to the acetylene absorber. The acetylene absorber is refluxed with NMP. Acetylene and gases with a solubility in N-methylpyrrolidone higher than the solubility of acetylene are practically completely absorbed from the gas mixture in the absorber. Synthesis gas leaves the absorber overhead. The solvent from the absorber bottom is sent to the top of I st. desorber under the pressure generated by pyrolysis gas. I st. desorber is operated at approximately atmospheric pressure. Circulating gas is discharged from top of I st. desorber. Acetylene contaminated with higher acetylenes is fed from II st. desorber to the bottom of I st. desorber. The concentrated acetylene free of higher acetylene homologues is discharged from the middle part of I st. desorber and goes to the acetylene washing tower for washing.

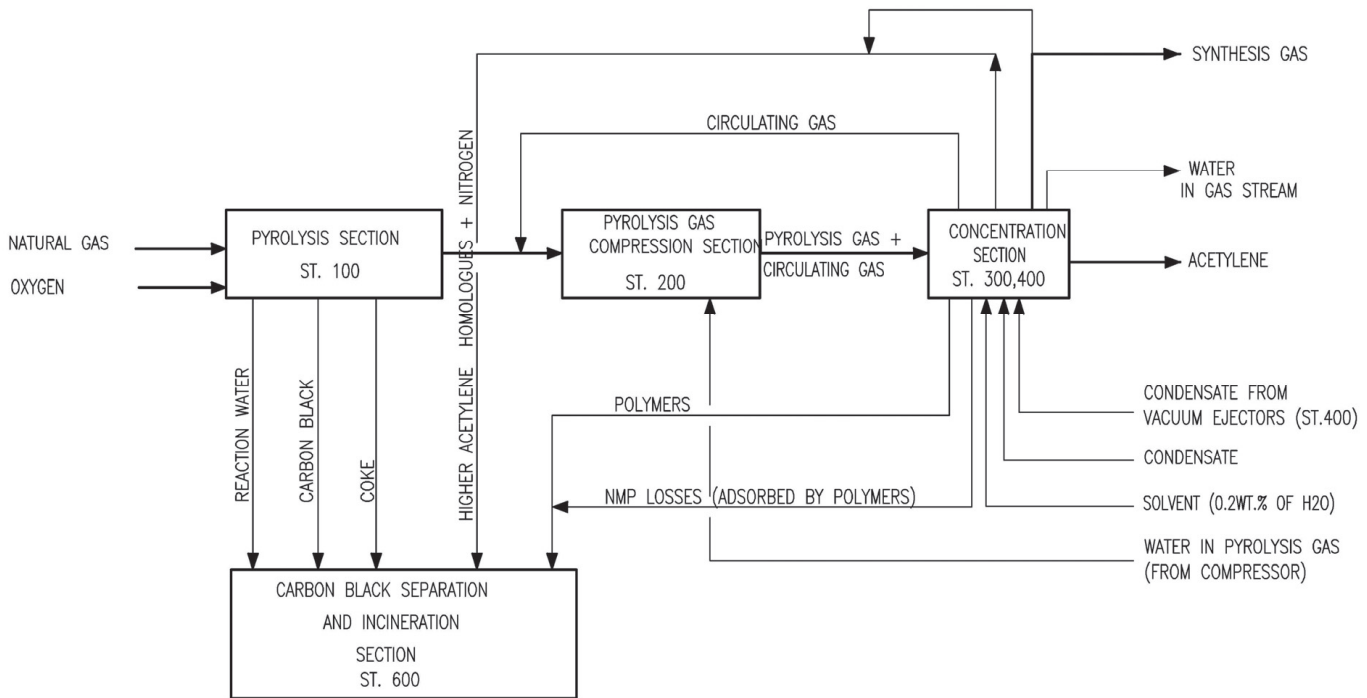
After washing-out of solvent vapor acetylene product is sent to the gas holder.

Solvent containing acetylene, higher acetylene homologues is discharged from bottom of I st. desorber. Solvent is sent to II st. desorber. II st. desorber consists of thermal desorber (top section) and vacuum desorber (bottom section).

In the thermal desorber and upper part of the vacuum desorber acetylene is desorbed from solvent. Crude acetylene from the vacuum desorber is supplied by vacuum compressor to the thermal desorber and then to bottom of I st. desorber.

The products of higher acetylenes polymerization are accumulated in the solvent during operation. In order to discharge polymers from the system a part of solvent is sent to the solvent regeneration unit.

BLOCK DIAGRAM OF ACETYLENE PLANT



## Services We Can Offer for This Technology

ALVIGO Holding can perform the following scope of works:

- preparation of investment feasibility study as applied to Client's conditions (for acetylene plant proper);
- Basic engineering design;
- Detail engineering design for all project parts including civil engineering design;
- Placement of orders for equipment manufacture with justification of selected vendors in Russia, CIS countries and other countries, preparation of pre-contract documentation;
- technical support during manufacture;
- designer's supervision during construction, erection;
- participation in startup and performance test.

### Acetylene. References.

Year	Project	Client	Services
2004	Detail design of automated process control system for operating acetylene plant	Russia, Nevinnomysk JSC "Nevinnomysk Asot"	Detail design
2005	Acetylene plant. Revamping of reaction block of pyrolysis section and acetylene purification system	Russia, Nevinnomysk JSC "Nevinnomysk Asot"	Detail design
2009	30000tpy natural-gas based acetylene plant	China, Luzhou, Sichuan Province, Sichuan Tianhua Fubang Chemical Co., Ltd	Basic design
2011	22000tpy natural-gas based acetylene plant	China, Baitao, Fuling, Chongqing Chongqing Ciyuan Chemical Material Co.,Ltd	Basic design
2012	60000tpy natural-gas based acetylene plant	China, Chongqing Chongqing Chemical& Pharmaceutical Holding (Group) Company, Ltd / Chongqing Changshou Chemical Co., Ltd	Basic design
2012	40000tpy natural-gas based acetylene plant	China, Suining, Sichuan Province Sichuan Tianfu Junan Industrial Co., Ltd	Basic design





## Caprolactam Production

Caprolactam is white crystals highly soluble in water, alcohol, ether and benzene. When heated with small amounts of water, alcohol, amines, organic acids and some other compounds, caprolactam polymerizes forming polyamide resin which is used for capron fiber production. An important property of caprolactam is a capability to polymerize forming valuable polymer – polycaproamide.

Caprolactam is used mainly for production of polyamide filaments and fibers as well as engineering plastics. The share of filaments and fibers is 60% of world demand, 34% are used for production of engineering plastics. The rest is used for fabrication of wrapping film and other materials.

Polyamide fibers and filaments are generally used for production of textiles, carpets, industrial filaments which are used, in turn, to manufacture tire cords. Tire yarn is the largest and rapid-growing segment of PA6 market.

In small amounts caprolactam can be used in polyurethane formation and lysine synthesis, fabrication of hard textile undercloth, film coatings, synthetic leathers, plastifiers and paint thinners.

Benzene, phenol, aniline, toluene are feedstocks for caprolactam production. Benzene is the most common feedstock in the world practice.

Benzene-based caprolactam process was developed in 1955 by Research Center GIAP. The first caprolactam plant based on cyclohexane air oxidation method using GIAP's technology was commissioned in 1963.

In subsequent years GIAP performed research and engineering works focused on updating the existing plants and designing the new improved plants. 10 caprolactam plants with 25000 tons and above capacity designed by GIAP were built and are successfully operated.

Phenol-based caprolactam plant designed by GIAP was also constructed.

All of these plants were designed and started up by GIAP's specialists. Equipment for caprolactam plants was supplied mainly by vendors of CIS countries; a part of specific types of compressors, pumps and valves was imported from other countries.

At present Alvigo's specialists actively work on improvement of existing plants by implementation of their developments to reach lower consumption figures as well as better environmental characteristics of the caprolactam plants.

### Caprolactam in solid crystalline or liquid form is a final product of the plant.

№	Specification		Grade	
			A	Б
1.	Permanganate index	PI	4.0 (max.)	7.0 (max.)
2.	Color of aqueous caprolactam solution with 50% mass fraction	Hazen color scale	3.0 (max.)	5.0 (max.)
3.	Volatile matters	mole/kg	0.4 (max.)	0.6 (max.)
4.	Crystallization temperature	°C	68.8 (min.)	68.8 (min.)
5.	Mass fraction of iron	%	0.00002 (max.)	0.00002 (max.)
6.	Mass fraction of cyclohexanone oxime	%	0.002 (max.)	0.002 (max.)
7.	Optical density of caprolactam solution with 50% mass fraction		0.04 (max.)	0.06 (max.)
8.	Acidity	mole/kg	0.1 (max.)	0.2 (max.)
9.	Alkalinity	mole/kg	0.05 (max.)	0.05 (max.)

The caprolactam plant includes cyclohexanone unit, hydroxylamine sulphate unit, caprolactam unit, ammonium sulphate unit and waste treatment unit.

### **Cyclohexanone Unit.**

Benzene-based cyclohexanone process has the following stages:

- Benzene hydrogenation. Stage 100.
- Cyclohexane oxidation. Stage 200.
- Oxidation and dehydrogenation products separation. Stage 300.
- Air and nitrogen compression. Stage 400.
- Intermediate storage. Stage 500.
- Catalytic treatment. Stage 600.
- Cyclohexanol dehydrogenation. Stage 700.

Benzene is hydrogenated by hydrogen to cyclohexane in vapor phase at 1.6-2.0MPaG and 150-230°C over nickel-chromium catalyst.

No by-products are formed during benzene hydrogenation. The quality of produced cyclohexane depends on quality of feed benzene and impurities it contains.

Produced cyclohexane is subject to rectification to remove high-boiling impurities came with benzene.

Bottoms of rectification column (heptane fraction) are plant waste.

Produced cyclohexane is oxidized by atmospheric oxygen to cyclohexanol and cyclohexanone under 0.8-1.2MPa pressure and temperature in the reaction zone of 150-160°C. At the same time a number of by-products including organic acids, esters and lower alcohols are formed.

The reaction products are neutralized by alkali and separated into organic and aqueous-alkaline layers. After distillation of unreacted cyclohexane the oxidation products are fed to the separation stage to separate final product.

In the separation stage, the oxidation products are treated first by an alkali for saponification of esters. After saponification the reaction mixture is separated into organic and aqueous-alkaline layers.

After saponification the mixture of organic products is separated by multistage rectification whereby final products of the unit – commercial cyclohexanol and cyclohexanone as well as organic wastes (alcohol fraction and x-oil) are produced.

In the air and nitrogen compression stage air used for cyclohexane oxidation and nitrogen required for startup of the unit, for purging in an emergency and for pressure test of the equipment are compressed.

Intermediate storage is designed to store cyclohexane, cyclohexanol, cyclohexanone, liquid drains and liquid organic wastes as well as to prepare cyclohexanol/cyclohexanone mixture used as raw material for adipic acid production.

After cyclohexane vapor removal by absorption off-gas of the cyclohexane oxidation stage is subject to catalytic treatment to remove some remaining organic impurities and carbon monoxide. Clean off-gas is discharged to atmosphere.

Cyclohexanol produced during cyclohexane oxidation is dehydrogenated by catalytic method to cyclohexanone which is then separated at oxidation products separation stage.

### **Hydroxylamine Sulfate (HAS) Unit.**

The hydroxylamine sulfate process comprises the following stages:

- Steam-oxygen ammonia conversion and nitrogen oxide production. Stage 100.
- Sulfuric acid purification. Stage 200.
- Hydrogen purification and hydroxylamine sulfate synthesis. Stage 300.
- Catalyst regeneration and preparation. Stage 400.

Pure nitrogen oxide is produced by catalytic steam-oxygen ammonia conversion at 900°C without pressure over platinum-rhodium catalyst.

The reaction heat is used to generate steam in a waste heat boiler. Steam mixed with gas is used instead of nitrogen as blanket gas to remove reaction heat.

Being purified, nitrogen oxide is sent to hydroxylamine sulfate synthesis.

Diluted pure sulfuric acid is cleaned using activated carbon from traces of impurities being poisons for

hydroxylamine sulfate synthesis catalyst.

Hydroxylamine is produced by catalytic reduction of nitrogen oxide with hydrogen at 40-45°C in the presence of suspended catalyst being platinum on the graphite support in diluted sulfuric acid.

Product solution is sent to catalyst recovery via filtration. Produced aqueous hydroxylamine sulfate solution is sent to the caprolactam unit to produce cyclohexanone oxime.

Due to deactivation the platinum catalyst used at stage 300 is subject from time to time to regeneration by its reduction. At the same time new active catalyst is prepared at stage 400.

### **Caprolactam Unit.**

The caprolactam process comprises the following stages:

- Cyclohexanone oximation with organics distillation and ammonium sulfate solution concentration. Stage 100.
- Rearrangement and neutralization. Stage 200.
- Caprolactam extraction and trichloroethylene regeneration. Stage 300.
- Caprolactam purification and separation. Stage 400.

Cyclohexanone oxime is produced by reacting cyclohexanone and hydroxylamine sulfate. To ensure rather complete conversion of cyclohexanone to oxime and reduce side reactions the process is run in two steps using countercurrent scheme within temperature range of 55-85°C.

The resulting cyclohexanone oxime is converted to caprolactam via Beckmann rearrangement by the action of oleum containing sulfur anhydride in a range of 19-24% by wt. at 110-130°C temperature.

Rearrangement products are neutralized using ammonia water with separation of lactam oil.

Caprolactam is separated from ammonium sulfate solution and lactam oil using trichloroethylene (TCE) followed by caprolactam reextraction from trichloroethylene by water.

Trichloroethylene is distilled from aqueous caprolactam solution and aqueous caprolactam solution is sent to the ion exchange treatment stage.

Ion exchange treatment reduces amount of impurities that affect final product quality characteristics – conductance, optical density and color of aqueous solution.

Then the aqueous solution is subject to concentration by evaporation, dewatering and vacuum distillation in thin-film rotary evaporators.

### **Ammonium Sulfate Unit.**

Процесс получения кристаллического сульфата аммония состоит из отделения выпарки водного раствора сульфата аммония и разделения суспензии, и отделения сушки влажных кристаллов сульфата аммония.

### **Waste Treatment Unit.**

The unit includes:

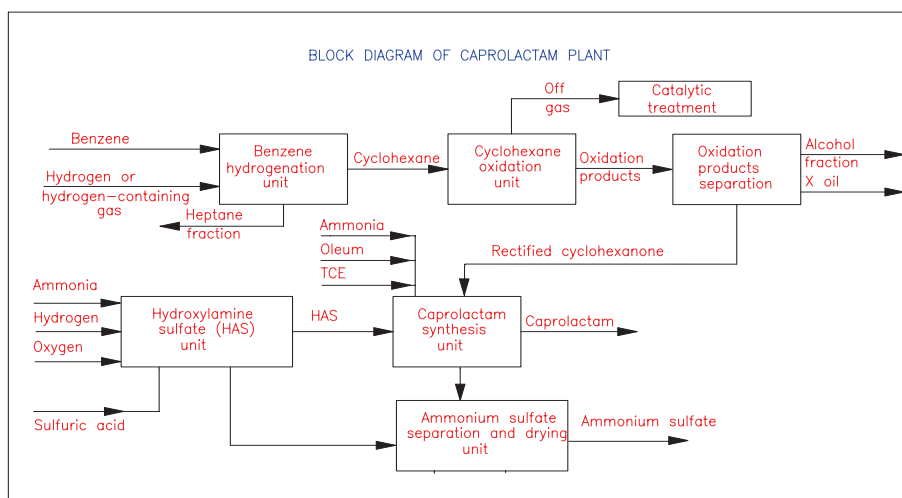
- Incineration units of the cyclohexanone and caprolactam units.
- Flare unit at stage 100.
- Flare unit at stage 200.

The cyclohexanone and caprolactam units produce gaseous and liquid effluents that are subject to thermal treatment: off-gas from stage 100, liquid organic wastes, aqueous acidic effluent and aqueous alkaline effluent, waste water.

These effluents are incinerated in incinerators of the cyclohexanone and caprolactam units, off-gas and organic wastes being used as fuel. Before being sent to the incinerators liquid wastes are stored in feed tanks of the unit.

Flare unit of stage 100 serves for combustion of off-gas of the stage at startup, shutdown of the stage and emergency shutdown of incinerator of the cyclohexanone unit. Combustible gases and vapors from safety valves of the stage and purge gases at shutdown of the stage are also sent to this flare unit for burning.

The flare unit at stage 200 is designed for burning of organic vapors discharged from safety valves of the stage and purge gas at shutdown of the stage.



## References

Country	Enterprise	City	Capacity, ths. tpy	Year of startup
RUSSIA	JSC "KuibyshevAzot"	Togliatti	50.0	1993
GEORGIA	JSC "Azot"	Rustavi	50.0	1987
UKRAINE	JSC "Azot"	Cherkassy	50.0	1985
BELARUS	JSC "GrognoAzot"	Grodno	50.0	1981
RUSSIA	JSC "KuibyshevAzot"	Togliatti	50.0	1974
RUSSIA	JSC "KemerovoAzot"	Kemerovo	48.0	1968
RUSSIA	JSC "ShchekinoAzot"	Shchekino	50.0	1966
UKRAINE	JSC "Azot"	Severodonetsk	25.0	1963

## ADIPIC ACID PRODUCTION

Adipic acid is a saturated dicarboxylic acid. These are colorless monoclinic crystals, readily soluble in alcohol or ether and hardly soluble in water.

Adipic acid is a multipurpose product ranking among 50 products of organic synthesis produced at the largest scale and the most important intermediate in the production of synthetic fiber nylon, polyhexamethylene adipamide, its esters, polyurethanes. It is used also as food additive E355.

Overwhelming volume of the produced acid is used both as raw material for production of polymer materials (polyamides, polyurethanes, polyesters) and auxiliary material for polymer chemistry - plasticizers.

The technology based on oxidation of cyclohexanol or its mixtures with cyclohexanone by nitric acid is leading one in the world industrial adipic acid production.

Cyclohexanol or its mixture with cyclohexanone is produced from benzene: benzene is hydrogenated to cyclohexane and cyclohexane is oxidized to cyclohexanol-cyclohexanone mixture.

For many years our company has carried out research and design activities with regard to oxidation of cyclohexanol and cyclohexanol-cyclohexanone mixture by nitric acid to adipic acid.

Based on in-house developments the Institute created an adipic acid plant including cyclohexanol-cyclohexanone mixture production from benzene and oxidation of this mixture to adipic acid.

Adipic acid plant based on this design is built and successfully operated in Rovno, Ukraine.

At present the specialists of our Institute continue the works aimed at upgrading of the existing adipic acid plants, reduction of consumption figures and improvement of environmental characteristics.

The quality characteristics of produced adipic acid are given below :

Characteristic	Norm
Mass fraction of adipic acid	min. 99.4%
Melting temperature	max. 151.5°C
Mass fraction of nitric acid	max. 0.001%
Mass fraction of iron	max. 0.0001%
Mass fraction of ash	max. 0.003%
Ass fraction of oxalic acid	max. 0.006%
Colour as per cobalt-platinum scale	max. 10

The adipic acid process comprises the following stages:

### 1. CYCLOHEXANOL/CYCLOHEXANONE PRODUCTION

Benzene-based cyclohexanol or cyclohexanol/cyclohexanone mixture production process comprises the following stages:

- benzene hydrogenation to cyclohexane;
- cyclohexane oxidation;
- oxidation products separation;
- air and nitrogen compression;
- intermediates storage;
- catalytic treatment.

Benzene is hydrogenated by hydrogen in a vapour phase at pressure of 1.5 - 2.0MPa, temperature of 130-230°C over nickel-chromium catalyst according to circulation scheme. Produced cyclohexane is subject to rectification to remove n-heptane and other impurities. Heptane fraction is a waste of the unit.

Cyclohexane is oxidized by atmospheric oxygen in a liquid phase at temperature of 150-165°C, pressure of 0.75-0.95 MPa in the presence of cobalt naphthenate catalyst. At the same time a number of by-products including organic acids, esters and lower alcohols are formed.

Cyclohexane oxidation products are separated by rectification with preliminary saponification of esters.

After saponification the reaction mixture is separated into organic and aqueous-alkaline layers. Organics mixture after saponification is separated by multistage rectification whereby final products of the unit - rectified cyclohexanol and rectified cyclohexanone - as well as organic wastes - alcohol fraction and x-oil - are produced.

In the air and nitrogen compression stage air used for cyclohexane oxidation and nitrogen required for startup of the unit, for purging in an emergency and for pressure test of the equipment are compressed.

Intermediates storage is designed to store cyclohexane, cyclohexanol, cyclohexanone, drained liquid, and liquid organic wastes as well as to prepare cyclohexanol/cyclohexanone mixture used as raw material for adipic acid production.

After cyclohexane vapor removal by absorption off-gas of the cyclohexane oxidation stage is subject to catalytic treatment to remove some remaining organic impurities and carbon monoxide.

## Consumption Figures per One Ton of Cyclohexanol:

### A. RAW MATERIAL

Benzene	1.1t
Hydrogen (H <sub>2</sub> 95% by vol.)	1080m <sup>3</sup>

### B. MATERIALS AND CATALYSTS

Sodium hydroxide (as 100% NaOH)	155 kg
Benzene hydrogenation catalyst	0.15 kg
Sulphur compounds adsorbent	0.081 kg
Gas desulphurization catalyst	0.14 kg
Cyclohexane oxidation catalyst	0.15 kg
Gas treatment catalyst	0.1 kg

## B. UTILITIES

Steam	
P=15 bar	4.2 t
P=10 bar	7.4 t
P=6 bar	0.9 t
Power	670 kWh
Cooling water ( $\Delta t=7^{\circ}\text{C}$ )	670 m <sup>3</sup>
Chilled water ( $\Delta t=5^{\circ}\text{C}$ )	22 m <sup>3</sup>
Nitrogen	370 m <sup>3</sup>
Instrument air	225 m <sup>3</sup>
Condensate	0.8 m <sup>3</sup>

## 2. ADIPIC ACID PRODUCTION

Adipic acid is produced by oxidation of cyclohexanol or its mixture with cyclohexanone by 40-55% nitric acid solution in the presence of ammonium metavanadate and copper nitrate as catalyst at temperature of 74-85°C and atmospheric pressure. The oxidation reaction produces heat.

Along with adipic acid small amounts of other dicarboxylic acids (succinic, glutaric, oxalic acids) as well as negligible amount of monocarboxylic acids (acetic acid, etc.) and nitrocompounds are formed.

In the course of cyclohexanol and cyclohexanone oxidation, nitric acid is reduced to nitrogen oxide and dioxide and dinitrogen oxide. The reaction mixture is stripped of nitrogen oxides using air.

Oxidation takes place in the reaction system consisting of oxidation reactor, stripping column, rectification column and maturing tank.

In the oxidation system there is a maturing tank in which reaction solution is held at elevated temperature before to be sent to crystallization, which prevents underoxidized organics from entering the crystallization stage.

Adipic acid is separated from the reaction mixture by vacuum crystallization. To produce adipic acid of the required quality the acid separated from aqueous solutions is subject to double recrystallization.

Crystalline adipic acid is separated from slurry in centrifuges. Drying and cooling of crystalline adipic acid are done by air in vessels with fluidized beds.

Dicarboxylic acids produced along with adipic acid are continuously discharged from the system. Dicarboxylic acids are separated from the mother liquor as a melt after additional adipic acid separation and nitric acid distillation. Dicarboxylic acids are crystallized and cooled in a roll crystallizer.

Waste water after floors flushing and equipment washing, that contains cyclohexanol and cyclohexanone, is sent to the waste treatment facilities.

## Consumption Figures per One Ton of Adipic Acid

### A. RAW MATERIAL

Cyclohexanol-cyclohexanone mixture (cyclohexanol content is min 65% by wt.)	0.77 t
Nitric acid (as 100%)	1.05 t

### B. MATERIALS AND CATALYSTS

Copper	0.55 kg
Ammonium metavanadate	0.55 kg
Caustic soda (as 100% NaOH)	50 kg
or Soda ash (as 100% Na <sub>2</sub> CO <sub>3</sub> )	66 kg

### C. UTILITIES

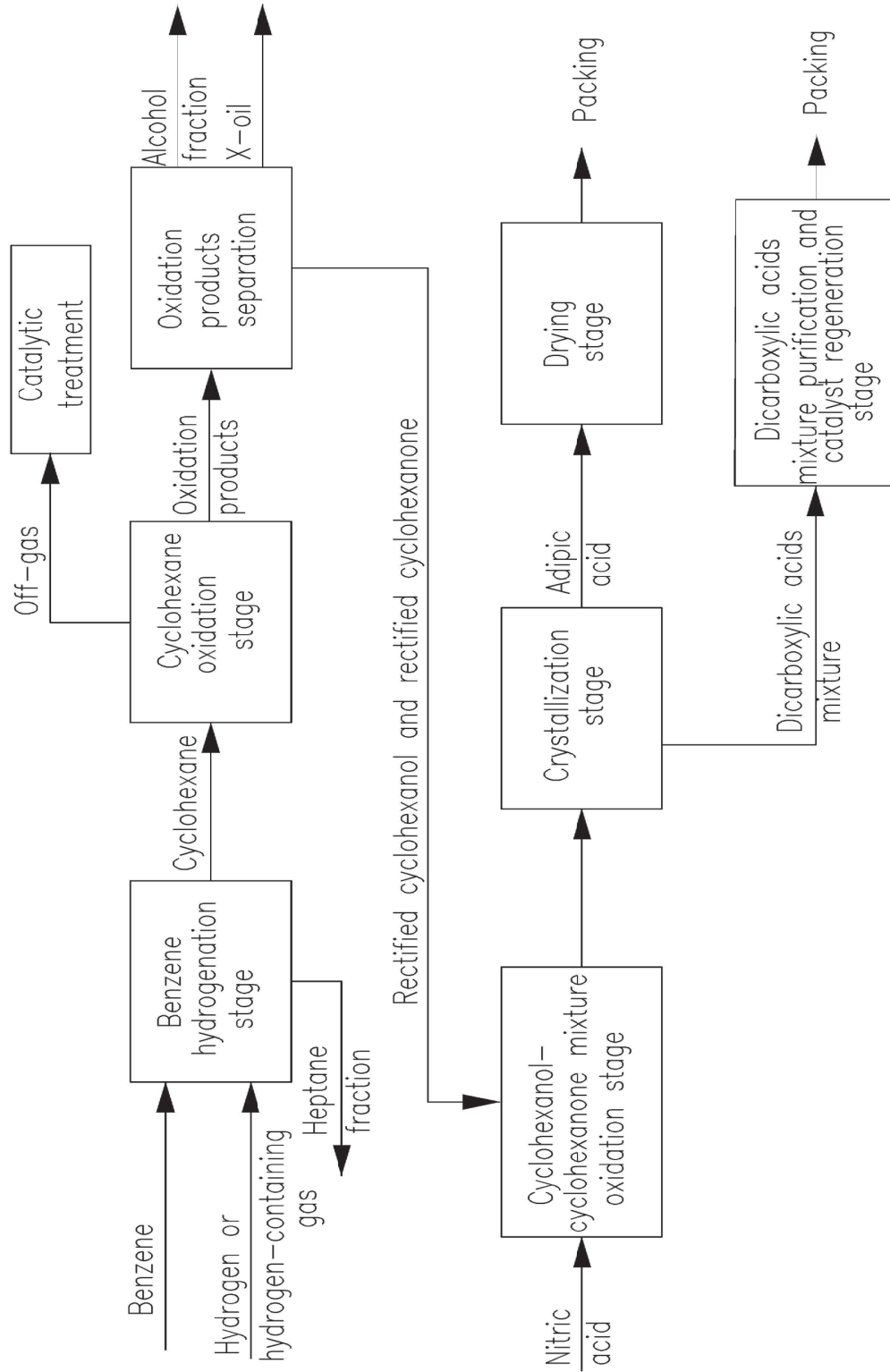
Steam	
P=18 bar	0.25 t
P=4.5 bar	6.1 t
Power	490 kWh
Cooling water ( $\Delta t=4^{\circ}\text{C}$ )	990 m <sup>3</sup>
Chilled water ( $\Delta t=4^{\circ}\text{C}$ )	61 m <sup>3</sup>
Nitrogen	320 m <sup>3</sup>
Instrument air	170 m <sup>3</sup>
Demineralized water	3.8 m <sup>3</sup>
Condensate	1.6 m <sup>3</sup>



## Brief Reference List

Year	Plant	Customer	Services
2006	Succinic acid and glutaric acid units based on purified mixture of lower dicarboxylic acids (LDA)	Ukraine, Rovno, JSC Rovnoazot	Basic Design. Technical assistance during construction and erection. Designer's supervision
2006	Unit for water washing-out of acids from oxidate and processing of aqueous-acidic layer to dicarboxylic acids mixture	Ukraine, Rovno, JSC Rovnoazot	Basic Design. Technical assistance during construction and erection. Designer's supervision
1998	Revamping of oxidation system of adipic acid plant	Ukraine, Rovno, JSC Rovnoazot	Detail Design. Startup, optimization of process conditions and designer's support during operation.
1998	LDA mixture purification unit (succinic, glutaric, adipic acids)	Ukraine, Rovno, JSC Rovno- azot	Basic Design. Detail Design. Technical assistance during construction and erection. Designer's supervision
1987	Hexamethylene diamine unit. AH-salt unit. SH salt unit	Ukraine, Rovno, chemical complex	Basic Design. Detail Design. Technical assistance during construction and erection. Designer's supervision
1984	KA oil- based adipic acid plant	Ukraine, Rovno, chemical complex	Technology development. Basic Design and Detail Design. Optimization of process conditions and designer's support during operation.
1976	Benzene-based adipic acid plant. Hexamethylene diamine unit. AH-salt unit	Ukraine, Severodonetsk, chemical complex	Acceptance of Basic Design developed by BASF (Germany). Basic Design and Detail Design for construction works, construction and erection supervision

**ADIPIC ACID PLANT. BLOCK FLOW DIAGRAM**



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