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Distillation – from Bronze Age till today

(extended abstract)

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Abstract

A short historical and pictorial excursion on distillation will be presented and new trends in development of distillation will be briefly discussed. The first distillation apparatus found in Mesopotamia (today´s Iraq) comes from the period 3500 BC. A part of distillation apparatus from Spišský Štvrtok (Slovakia) which dates back to 1500 BC (Bronze Age). It is supposed to be the oldest part of a distillation apparatus not only on territory of Slovakia but most likely in Europe. One of the first books on distillation written by J. French have been published in London in 1651.

Industrial application other than ethanol distillation was distillation of tar and producing highly purified tar components such as anthracene, carbolic acid and benzene developed by Raschig in Germany who developed also the first modern random packing Raschig rings. Petroleum refineries were next wide application of distillation where this unit operation and related equipment were developed to today´s matured state. The first petroleum refinery Apollo in Bratislava was founded in 1895 and started operation in April 1896. During the first year of operation treated 23 560 ton of crude oil. A new refinery have been built in Bratislava with start up in 1957 and capacity of 120 000 ton per year. Present two distillation units have capacity 2 million ton/year each.

New processes as extractive distillation and membrane distillation were developed and hybrid systems with distillation combined with membrane separations are under development may bring new impulse to distillation applications.

Bronze Age

„Bronze Age – the first golden age of Europe“ was a campaign initiated and supported by European Council started in 1994. In the Bronze age, which lasted in Europe about 2000 years, were led bases of European civilisation and ethnic societies in today's Slovak territory actively participated in this process [1]. Rich discoveries of ceramic and metallic objects document high level of development in our territory. These were presented in very successful exhibition "Golden age in Carpathian mountains“ prepared by Archaeological Institute of Slovak Academy of Sciences and installed in Fiorano Modenese in Italy in 2002 and further transferred to two other Italian cities Legnano and Bondeno and in 2004 continued in three Slovak cities including Bratislava with catalogue [1].

The first distillation apparatus have been found in Tepe Gaura in Mesopotamia (today´s Iraq) comes from the period 3500 BC, Fig. 18 in book [2] shown in Fig. 1. A part of distillation apparatus from Spišský Štvrtok (Slovakia) which dates back to 1500 BC is shown in Fig. 2a and its reconstruction (upper part was not found) [3] is in Fig. 2b. It is supposed to be the oldest part of a distillation apparatus not only on territory of Slovakia but most likely in Europe [3]. It is obvious that both vessels are variants of the same type of still where function and efficiency had been maintained despite size of vessel from Spišský Štvrtok is smaller with height of bottom part of 35 cm comparing to 48 cm for vessel from Tepe Gaura [3].

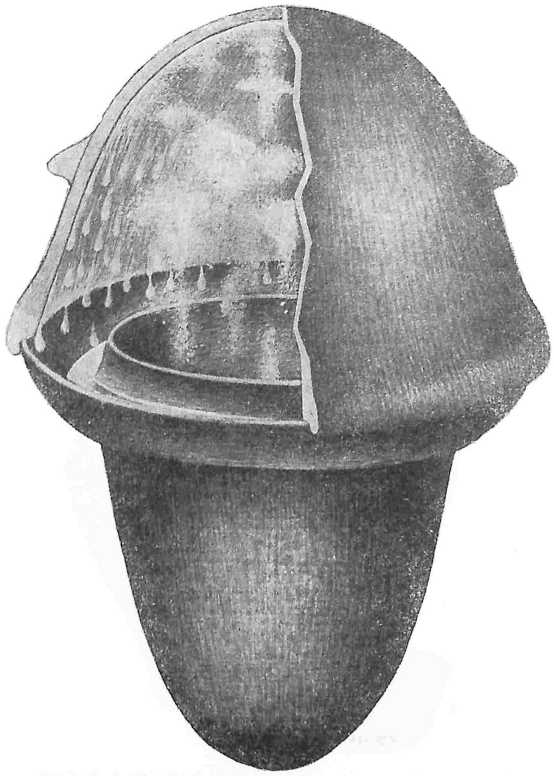

Fig. 1. Reconstruction of a distillation apparatus from Tepe Gaura in Mesopotamia (today Iraq) [3].

(a) (b)

Fig. 2. A bottom part (boiler) of distillation apparatus from Spišský Štvrtok (Eastern Slovakia) [1] (a) and its reconstruction (upper part (condenser) was not found) [3] (b).

Late Antiquity

Zosimos of Panopolis was an Egyptian or Greek alchemist and Gnostic mystic from the end of the 3rd and beginning of the 4th century AD. (Wikipedia)

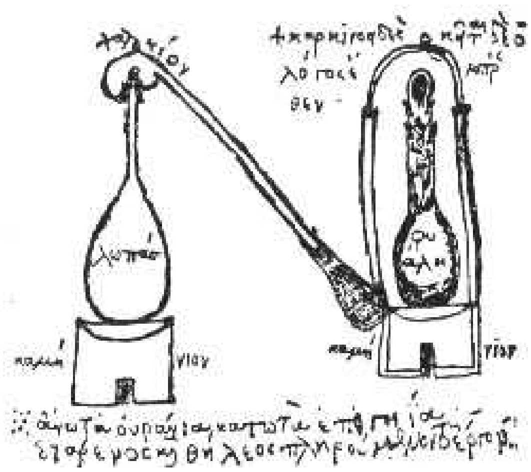

Fig. 3. Distillation apparatus of Zosimos, from Marcelin Berthelot, *Collection des anciens alchimistes grecs* (3 vol., Paris, 1887-1888).

Medieval time

The earliest distillation of Attar was mentioned in the Hindu Ayurvedic text Charaka Samhita. The Harshacharita, written in 7th century A.D. in Northern India mentions use of fragrant agar wood oil. (Wikipedia, history of perfume)

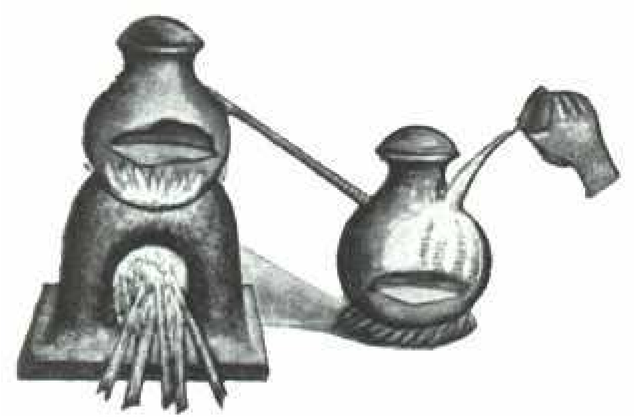

Fig. 4. Distillation apparatus using simple hand cooling for the receiver.

Arab scientists

The birth of the Arab physical sciences in the 7th and 8th centuries was one more expression of the same breakthroughs that were happening in Arab mathematics, astronomy and geography, driven partly by long-standing scientific traditions in the peoples who came into the Arabic caliphate. Perhaps the Arab scientific field where the birth was most dramatic was in chemistry. And the earliest and most powerful Arab practitioner of the new science of chemistry was Jabir Ibn Hayyan, recruited by Caliph Harun Al Rashid to work in the early House of Wisdom in Baghdad.

Jabir Ibn Hayyan (Geber, 721-815) was a prominent Islamic alchemist, pharmacist, philosopher, astronomer, and physicist [4]. He has also been referred to as "the father of Arab chemistry" by Europeans. Jabir is mostly known for his contributions to chemistry. He emphasised systematic experimentation, and did much to free alchemy from superstition and turn it into a science. He is credited with the invention of many types of now-basic chemical laboratory equipment, and with the discovery and description of many now-commonplace chemical substances and processes - such as the hydrochloric and nitric acids, *distillation*, and crystalization that have become the foundation of today's chemistry and chemical engineering. Jabir is also credited with the invention and development of several chemical instruments that are still used today, such as the *alembic*, which made distillation easy, safe, and efficient. He noted that boiling wine released a flammable vapor, *thus paving the way to Al-Razi's discovery of ethanol*.

Fig. 5. Alchemist Jabir helped lay the foundation of modern chemistry.

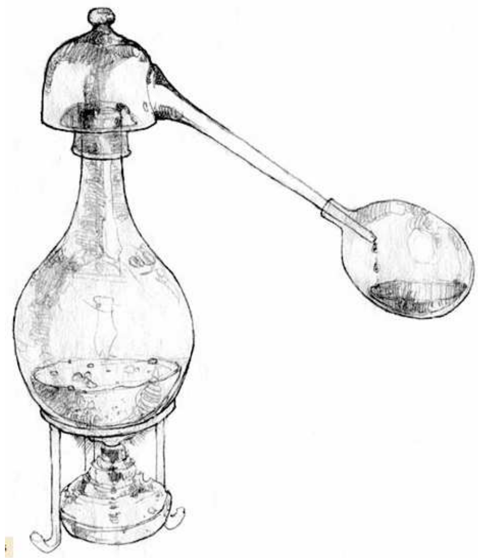

Fig. 6. Early Arab distillation device (alembic), used by early chemists like Jabir and Al Razi.

Fig. 7. Distillation in medieval time.

Fig. 8. Traditional Alembic Pot Still produced nowadays for home use http://www.essentialoil.com/alembic5.html .

Al-Razi (865-925) was the preeminent Pharmacist and physician of his time [5]. The discovery of alcohol, first to produce acids such as sulfuric acid, writing up extensive notes on diseases such as smallpox and chickenpox, a pioneer in ophthalmology, author of first book on pediatrics, making leading contributions in inorganic and organic chemistry, also the author of several philosophical works.

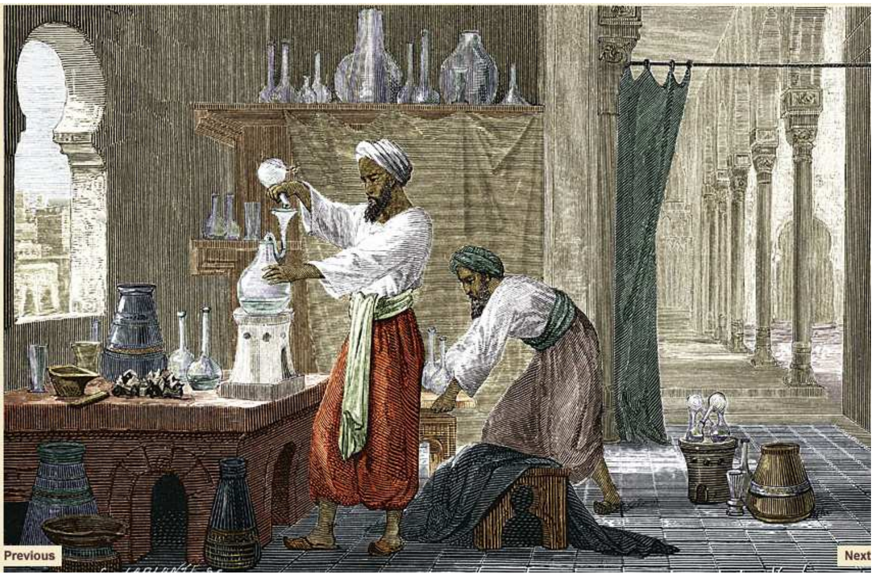

Fig. 9. Chemist physician Al Razi at work in his laboratory

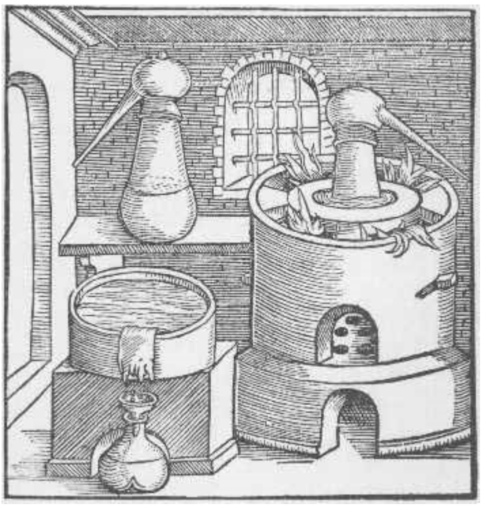

Fig. 10. Distillation in Al-Razi time.

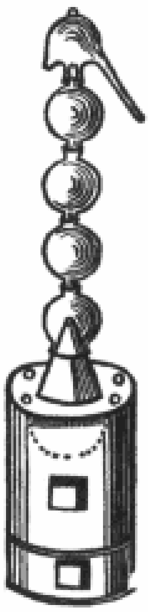

Fig. 11. Circular furnace with fractional distillation apparatus (Abraham Elezar pseud., from A. Crusius Erfurt 1735).

Al-Kindi (801-873, Baghdad, Iraq) [6]

He wrote in the 9th century a book on perfumes which he named '*Book of the Chemistry of Perfume and Distillations*'. It contained more than hundred recipes for fragrant oils, salves, aromatic waters and substitutes or imitations of costly drugs. The book also described one hundred and seven methods and recipes for perfume-making, and even the perfume making equipment, like the *alembic*, still bears its Arabic name.

Avicenna (Ibn Sīnā, 980- 1037, Persia, Afghanistan) [7]

Avicenna created an extensive corpus of works during what is commonly known as Islam's Golden Age, in which the translations of Greco-Roman, Persian and Indian texts were studied extensively. Greco-Roman (Mid- and Neo-Platonic, and Aristotelian) texts by the Kindi school were commented, redacted and developed substantially by Islamic intellectuals, who also built upon Persian and Indian mathematical systems, astronomy, algebra, trigonometry and medicine.

In chemistry, the chemical process of *steam distillation was first described by Avicenna*. The technique was used to produce alcohol and essential oils; the latter was fundamental to aromatherapy. *He also invented the cooling coil, which condenses the aromatic vapours*. This was a breakthrough in distillation technology and he made use of it in his steam distillation process, to produce essential oils. He first experimented with the rose. Until his discovery, liquid perfumes were mixtures of oil and crushed herbs, or petals which made a strong blend. Rose water was more delicate, and immediately became popular. Both of the raw ingredients and distillation technology significantly influenced western perfumery and scientific developments, particularly chemistry. As a chemist, Avicenna was one of the first to write refutations on alchemy, after al-Kindi.

One of the first books on distillation "The art of distillation" written by J. French have been published in London in 1651 [8].

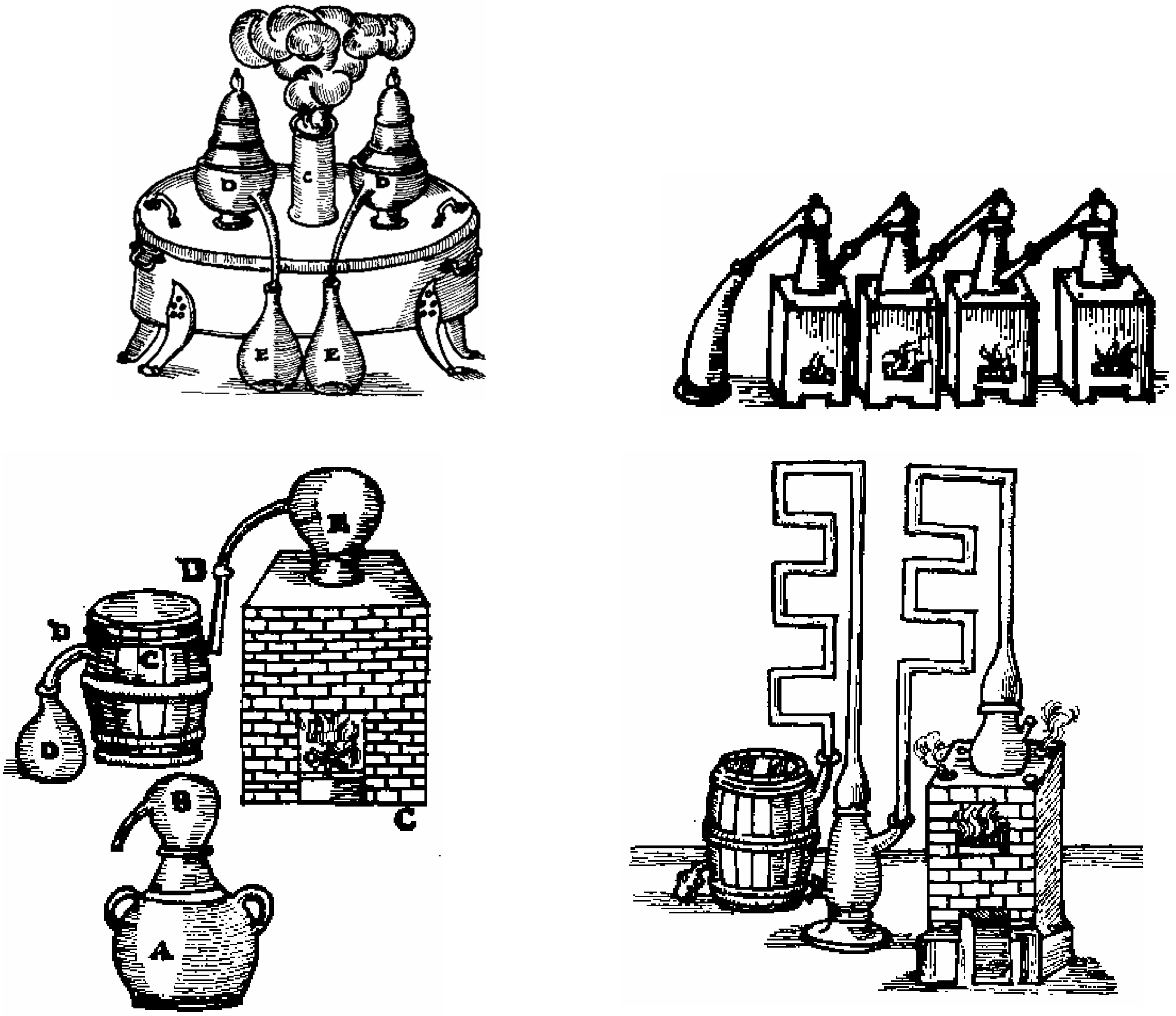

Fig. 12. Figures of distillation apparatus from J. French book [8].

19th and 20th century

In preindustrial era until the 19th century, renewable raw materials were the major source of energy and material use. During the Industrial Revolution, the use of coal increased sharply and coal quickly becomes a key raw material in the chemical industry and energy production.

Industrial application other than ethanol distillation was distillation of tar and producing highly purified tar components such as anthracene, carbolic acid and benzene developed by Raschig in Germany who developed also the first modern random packing Raschig rings, Fig. 14. In the 20th

Fig. 13. Fritz Raschig

Fig. 14. Ceramic Raschig rings

century, there has been a changeover in fossil fuel sources from coal to crude oil and natural gas due to lower prices, simpler logistics and the versatility in usage of oil and gas. Petroleum refineries and petrochemical plants were typical with wide application of distillation where this unit operation and related equipment were developed to today´s matured state.

The first petroleum refinery Apollo in Bratislava was founded in 1895 and started operation in April 1896 [9]. During the first year of operation treated 23 560 ton of crude oil. Refinery was renamed to Slovnaft in 1949. A new refinery have been built in Bratislava with start up in 1957 and capacity of 120 000 ton per year. Present two distillation units have capacity 2 million ton/year each.

Fig. 15. Atmospheric-vacuum distillation of crude oil in Apollo.

Fig. 16. Apollo distillation after American bombardment in June 1944.

Fig. 17. Atmospheric-vacuum distillation 3 of crude oil in Slonaft with capacity of 1.3 mil ton/year after intensification.

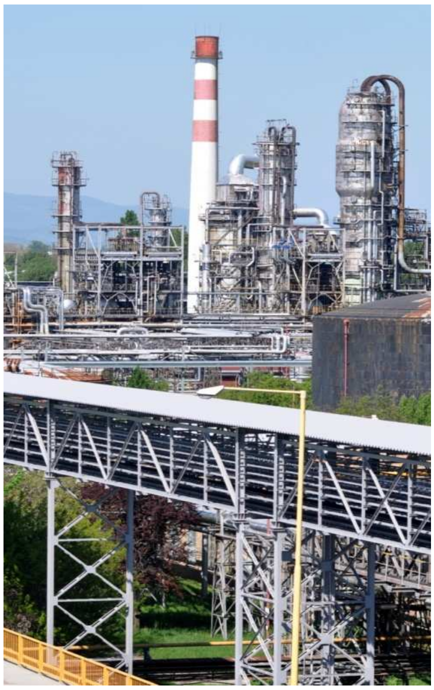

Fig. 18. Atmospheric-vacuum distillation of crude oil in Slonaft with capacity of 2 mil ton/year.

Desalination of sea water

Scarcity of drinking water in large territories requires its production from available sources like brackish water or sea water. One possibility is to use distillation and multi-stage flash distillation (MSF) was developed which scheme is shown in Fig. 19. Like all evaporative processes, MSF can produce high-quality fresh water with very low salt concentrations (10 ppm or less), from salt concentrations as high as 60,000 to 70,000 ppm total dissolved solids, nearly twice the salinity of seawater. In MSF, evaporation or "flashing" occurs from the bulk liquid. This minimizes scale and is a major reason MSF has been popular for several decades. Generally, only a small percentage of feed water is converted to water vapour in one stage, depending on the pressure maintained in each stage. MSF plants may contain between 4 and 40 stages, but most typically are in the range of 18 to 25. Multi-stage flash plants are typically built in sizes from 10,000 m^3/day to over 35,000 m^3/day, with several units grouped together. MSF accounts for the greatest installed thermal distillation capacity [10-11]. As of early 2005, the largest MSF plant in operation was in Shoaiba in Saudi Arabi [12]. This plant desalinates seawater for municipal purposes with a total capacity 455,000 m^3/day, see Fig. 20.

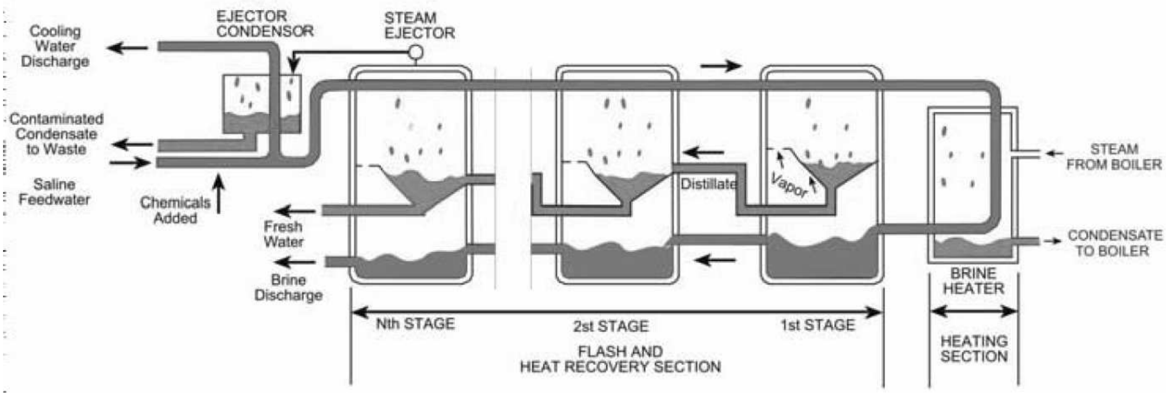

Fig. 19. Simple scheme of multi-stage flash distillation process [11].

Fig. 20. Multi-stage flash distillation (MSF) desalination plant in Shoaiba currently as the largest in the world [12].

21th century

Historical milestones of distillation development are summarised in Table 1. In connection with the limited availability and increasing price of crude oil and natural gas, the question now arises how to face this situation and what raw material base will develop in the future? Biomass as a renewable raw material could be answer [13-14]. There is a historical line of dominant resources used from local renewable resources to coal, coal gas and tar industries to crude oil and natural gas in petroleum refineries and petrochemical industry and recently switch to biomass in biorefineries and other renewable resources is of increased importance.

Transformation of raw material platform to biomass will not be quick and simple. It requires concerted cooperation of several scientific disciplines as agriculture, forestry, biology, biotechnology, chemistry, chemical engineering, environmental sciences, but also industrialists, strong economical and political impulse, etc. Renewable raw materials will be increasingly used in the future. New processes have to be developed to transform biomass to fuels, energy and chemicals in economically competitive way. This will be a challenge also for distillation especially in hybrid systems.

Table 1. Milestones of distillation development.

Date	Process/equipment	Scientist	Reference
3500 BC	Ceramic distillation apparatus from Tepe Gaura in Mesopotamia (today´s Iraq)		[2-3]
1500 BC	Ceramic distillation apparatus from Spišský Štvrtok (Slovakia)		[1, 3]
801-873	Book of the Chemistry of Perfume and Distillations	Al-Kindi	[6]
721-815	Developed alembic distillation apparatus, identified flammable vapours when distilling wine.	Jābir ibn Hayyān	[4]
865-925	He is known to have perfected methods of distillation and extraction, which have led to his discovery of sulfuric acid and alcohol.	Al-Razi	[5]
980- 1037	Steam distillation was first described. He invented the cooling coil to condense vapours from distillation	Avicenna (Ibn Sīnā)	[7]
1651	One of the first books on distillation was published	French, J.,	[8]
End of 19th century	Industrial distillation of tar		http://www.raschig.de/Company-en
End of 19th century	First modern random packing for distillation columns	Raschig	http://www.raschig.de/Company-en
Beginning of 20th century	Development of several stage evaporators in sugar industry		
20th century	Development of distillation for petroleum refineries and petrochemical plants. Bubble-cap trays and packed columns were mostly used initially.		
50-ties	Valve trays and structured packings instead of random packings were introduced.		
60-ties	High capacity multi-stage flash distillation (MSF) and multiple-effect distillation (MED) equipment have been developed sea water desalination		[10-11]
80-ties	High capacity and highly efficient trays have been developed		
21th century	Hybrid distillation and membrane separation processes are under development for bioethanol dewatering		[15-18]
21th century	Membrane distillation process is under development.		[19-22]

New developments in distillation

Modern civilisation faces several challenges among them shortage of water in many areas, shortage of fossil raw materials with need to switch fuel and chemical industry to renewable resources and environmental aspects of our civilisation connected with changes of climate.

Membrane distillation

Membrane based distillation has potential to improve economy of sea water desalination. Recent research results gives impulse for further development [19-23].

Extractive distillation of ethanol.

For fuel applications, ethanol essentially free of water has to be produced. Considering the low concentration achieved during fermentation, a huge separation effort has to be expected. In addition, an azeotrope is formed in this system, which cannot be further separated by simple distillation. Entrainers, which are fed in counter-current into the separation column, are hence chosen to interact selectively with the high-boiling component, in this case water, thus reducing its activity and increasing the relative volatility of ethanol. A high capacity is also important to keep the column diameter to a minimum. Entrainers enhance the separation factor, and the ionic liquid [C2mim][BF4] is more efficient than ethanediol if similar concentrations are used. The use of an ionic liquid entrainer reduces thus the number of plates and/or the recirculation ratio, leading to overall reduced separation costs [24]. Ionic liquids may provide higher energy efficiency than other methods.

Hybrid systems with distillation

Hybrid systems with distillation and vapour permeation shows promising results in decreasing energy demand for bioethanol dewatering for fuel applications [15-18, 25]

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