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Current trends in the world market of precious metals

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Annotation. *The market of precious metals in the world is studied. The requirements for the standard of gold, silver and platinum ingots are named. Factors influencing the world market of precious metals are revealed. Forms of market organization are described. The dynamics of gold, silver, platinum and palladium production in 2010 - 2019 are given. The tendencies of development of the world market of precious metals and the market of precious metals in Ukraine are named.*

KEYWORDS: GOLD, SILVER, PLATINUM, PALADIUM, PRICING, PRODUCTION

1. Introduction

Precious metals (gold, silver, platinum and palladium) are a specific type of financial asset and are one of the most popular investment instruments. The development of this segment of the financial market directly affects the financial and investment opportunities of the country, which it is able to realize, using the mediation of both its own financial institutions and relevant structures with foreign capital. A sufficient reserve asset of precious metals makes it possible to increase both the political and foreign economic and social advantages of a country in the international arena.

Obviously, the individual reserves of precious metals of each country are formed, primarily, depending on its financial and economic condition, as well as changes in exchange rates. Therefore, we can talk about the mutual influence of the precious metals market and other subjects of the national economy.

The aim of the article is to identify current trends in the precious metals market based on the analysis of the world precious metals market and to consider the problems and prospects of the Ukrainian precious metals market.

2. The market of precious metals in the world

There is a distribution of gold markets, which depends on the degree of government regulation. In this case, there are four categories of markets [1]:

1. World - such markets are in London, Chicago, Zurich, Frankfurt and Hong Kong;
2. Internal free - their location in Milan, Paris and Rio de Janeiro;
3. Local controlled - located in Athens and Cairo;
4. "Black" markets - the main one is in Bombay.

According to experts, more than 180,000 tons of gold have been mined on Earth. The vast majority of all mined precious metal is presented in the form of jewelry and this share is about 40%, also a significant share of mining is in state reserves - 30%, no less significant share of gold is stored in bullion and coins - 20% and the last 10% are used in industry. Most of this precious metal is consumed by countries in Asia because of their culture and customs. The increased demand for gold products in these countries is mainly due to low cost and increased solvency.

There are two main participants in the precious metals market - market makers and brokerage offices. Each of them performs certain functions and represents:

1. From sellers:
 - various corporations engaged in the gold mining industry;
 - refining productions for processing scrap from gold;
 - state reserves of national banks, which reduce the reserves of precious metals that were accumulated earlier;
 - speculators and hedgers, whose job is to speculate on precious metals contracts (mainly forward, option and futures contracts);
 - private hoarders and investors, whose task is to sell previously accumulated reserves of precious metals.
2. From buyers:

- various industrial and technical productions using precious metals;
- jewelry industrial production;
- dentistry;
- investors or investors' agents (commercial banks);
- state reserves of central banks;
- private hoarders (for example, they can be collectors of gold coins or ingots).

To sell precious metals on the market, they must meet the International Quality Standards adopted by the London Precious Metals Market Association (LBMA), which are marked in the association's documents as the "London good delivery" standard and have the following requirements [2]:

- 1) For gold bars:
 - Weight of pure gold ingot - from 350 to 450 troy ounces (from 10886 to 13754 grams);
 - The weight of each ingot can be expressed in Aryan ounces and be a multiple of 0.025 ounces;
 - Purity of the metal - not less than 995 parts of chemically pure gold per 1000 parts of ligature weight.

The ingot must bear the following mandatory marks: serial number, sample, manufacturer's mark and year of manufacture of the ingot (the requirement has been in force since 1988).

The ingot should be without indentations, not be porous and have other defects. It should be comfortable to carry and store.

- 2) For silver ingots:
 - Ingot weight from 500 to 1250 troy ounces (from 15552 to 38879 grams);
 - The weight of each ingot must be expressed in Aryan ounces and be a multiple of 0.10 ounces;
 - The purity of the metal must be at least 999 parts of pure chemical silver per 1000 parts of ligature weight.

The ingot must bear the following mandatory marks: serial number, sample, manufacturer's mark and weight in Aryan ounces or kilograms (if the weight of the ingot is in kilograms, it must be converted to troy ounces and meet the above requirements).

The ingot must be of the correct shape, as well as easy to carry and transport, and must not contain defects. Another requirement is that the edges of the ingot must be straight and not sharp.

- 3) For ingots (plates) of platinum:
 - Weight of the ingot (plate) - from 32,150 to 192,904 troy ounces (from 1000 to 6000 grams);
 - The purity of the metal must be at least 999.5 parts of chemically pure metal per 1000 ligature weight.

Such ingots also have a number of features related to special labels: serial number, sample, letters PT or PLATINUM, brand of the manufacturer, as well as weight in grams or Aryan ounces.

3. Factors influencing the world market of precious metals

Today in practice various forms of the organization of the market of precious metals [3] become widespread:

- first of all, it is a market that is strictly regulated by the state
- the main and only buyer and seller of precious metals in such a market are central banks, and all other market participants already buy metal from them (China, South Africa);

- the next form of roar is trading in precious metals through specialized exchanges or sections of commodity or currency exchanges. Regulation of operations, access to non-residents is carried out by central banks (France, Turkey);

- there is also a system of free exchange trade in precious metals (Hong Kong, Luxembourg, USA);

- another form is the trade in precious metals, which is carried out by several large monopoly banks or their associations (UK, Germany, Switzerland);

- a system of competitive interbank trading, dominated by several banks- "market makers" (Japan, Holland and the United States).

In some countries, there may be several forms of trade in precious metals at the same time, but only those countries can afford this, which have fairly liberal legislation that allows all forms of trade to develop competitively.

As for the direct factors, they include industrial demand as a catalyst for changes in the value of various precious metals. The largest consumers of precious metals are usually the electrical industry, mechanical engineering, jewelry and many others. We can also include the economic and political situation of the world's leading countries, in particular, the United States.

Gold mining is growing every year, and a graph can be seen in Figure 1, which shows the dynamics of this precious metal over the past five years.

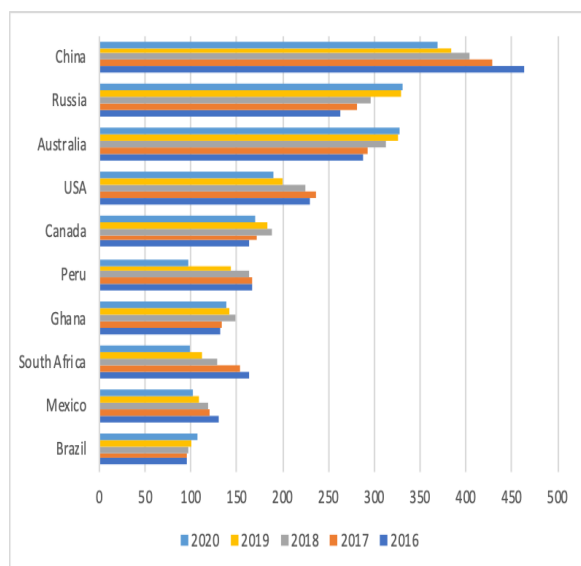


Fig. 1. Dynamics of gold production by leading countries in 2016-2020.
Source: compiled on the basis of [4].

As of 2019, the volume of silver production increased by 27 thousand tons. Due to the growing consumption of jewelry, silver coins still have a surplus of this precious metal. For example, we can consider a dozen leading countries in silver mining (Fig. 2).

Platinum is one of the rarest metals in the world. The five countries, namely the United States, Canada, Zimbabwe, Russia and South Africa, account for 97% of the world's world platinum. The dynamics of platinum production in 2010-2019 is shown in Fig. 3.

Palladium belongs to the platinum group and is chemically similar to it. It is most often used in catalytic converters, which is a key component of internal combustion engines, which are equipped with most motor vehicles in the world. Every year the dynamics of palladium production changes slightly (Fig. 4).

Indirect factors influencing the price of precious metals are, first of all, the price of oil. According to research, with the rise in oil prices by 1 US dollar, the price of gold increases by an average of 1.6 US dollars, and silver rises by 0.06 US dollars [8]. Also affected by changes in the US dollar, stock indices of global financial markets, the impact of prices on other precious metals. Schematically, the mechanism of the pricing process in the world market of precious metals is shown in Fig. 5.

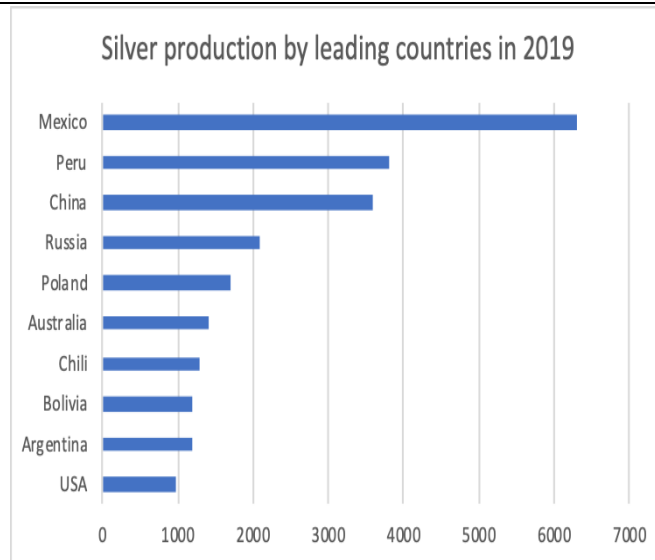


Fig. 2. Volumes of silver production by leading countries in 2019, vol.
Source: compiled on the basis of [5].

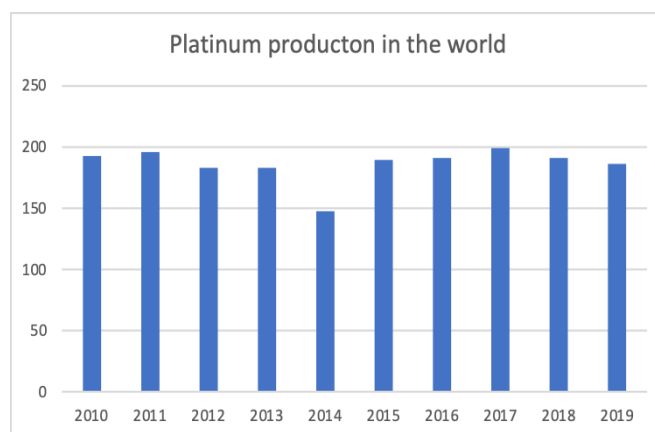


Fig. 3. Dynamics of platinum production in the world 2010-2019, vol.
Source: compiled on the basis of [6].

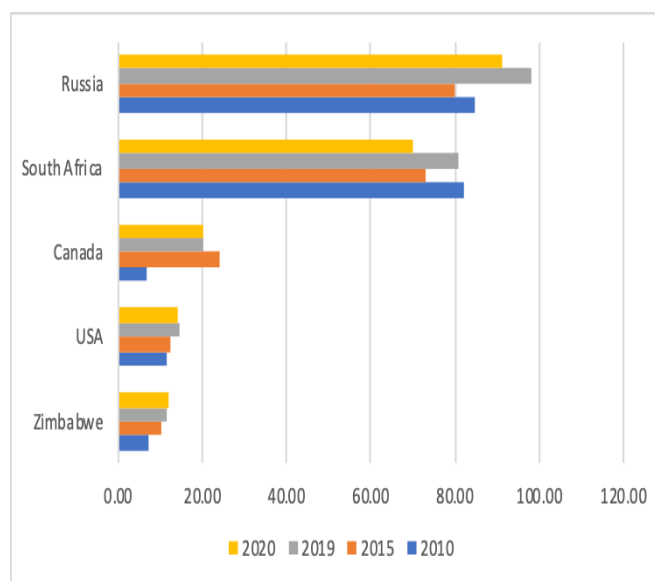


Fig. 4. Dynamics of palladium production in different countries 2010-2020.
Source: compiled on the basis of [7].

Gold can be called the most liquid asset, due to its increased sensitivity to financial and economic changes (mainly due to rising

or falling interest rates in the US). In addition, it depends significantly on the world's leading currencies.

The price of gold is growing every year. In light of recent events in the world, the rise in gold prices is due to the cessation of mining and measures by the US Federal Reserve, which are aimed

at supporting the international economy as a result of the crown virus pandemic. Due to the fact that China is successfully fighting this disease, the quotations of this precious metal may eventually decrease.

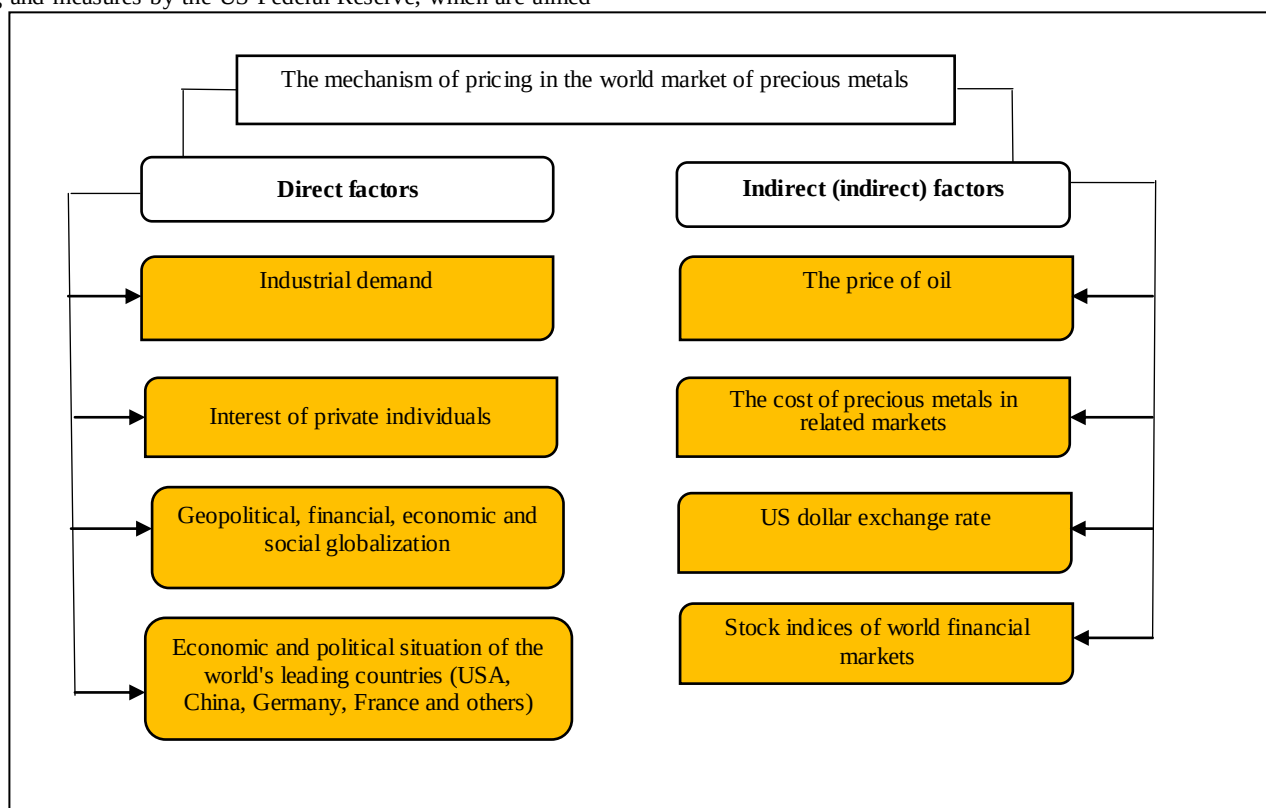


Fig. 5. The mechanism of formation of prices for precious metals.

On March 25, 2020, the price of gold reached a record high due to panic in the market as a result of the crown virus. In monetary terms, the price increase was the highest in the history of observations. The price of gold on March 25, 2020 on the New York Stock Exchange SOMEH as of 12:00 was 1654.32 US dollars per ounce.

Silver is also reacting painfully to the current situation on the stock market and the fight against the pandemic. But not everything is so simple here. The fact is that on March 16, 2020, the value of silver per 1 ounce was 11.8 US dollars - the lowest figure in 10 years. The significant decline in value was due to risk assessments by investors and the fact that they began to prefer a more reliable metal, such as gold, as well as US and UK government bonds. Over time, the price rose slightly, but not significantly. As of March 25, 2020, at 12:00, an ounce of silver could be purchased on the SOMEH exchange for \$ 14.62.

If we talk about trade in platinum, the main factor influencing the exchange rate is the balance of supply and demand. Platinum has certain features that affect the popularity of this metal in various industries. About 40% of this metal is used by the machine-building industry. In contrast to gold, which can be mined in pure form, platinum can exist only in the form of an alloy with other metals, and the process of its separation is quite complex and energy consuming. Platinum is also significantly added in value, as are other precious metals. On February 25, 2020 on the NYMEX exchange as of 12:00 the value of one ounce was 968.95 US dollars, and on March 25, 2020 this figure decreased significantly and amounted to 724, 22 US dollars per ounce.

The cost of palladium on March 25, 2020 at 12:00 was 1936.58 US dollars per ounce. Compared to the previous month, the price decreased by as much as 722.22 US dollars (-27.16%). At the end of February of the same year, an ounce of palladium was worth \$ 2,658.80.

The general dynamics of world prices for precious metals for 2011-2021 (Fig. 6) shows that the most stable is gold, which is not going to give up its position, and its temporary decline in value is quite short-term, which once again confirms the importance of this metal in social and economic relations at the international level.

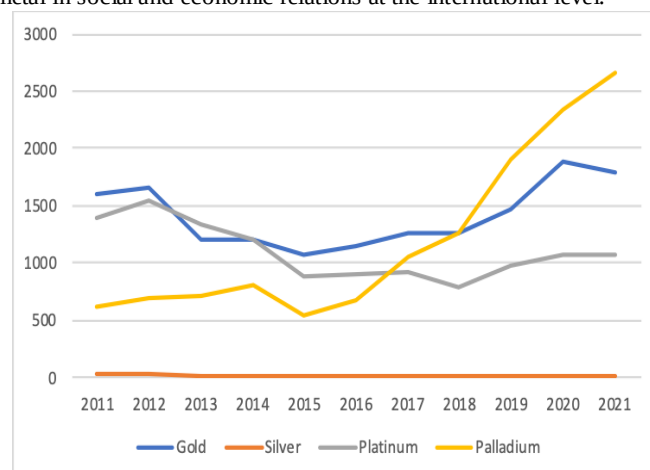


Fig. 6. Dynamics of prices for precious metals in the period from 2011 - 2021, \$ / ounce

Source: compiled on the basis of [10, 11, 12, 13].

4. Trends in the world market of precious metals

An important means of combating inflation is the interdependence of currencies and precious metals, but the instability of prices for precious metals can lead to economic crises,

and therefore they (precious metals) should not always be used as an indisputable measure for other goods.

Trading in precious metals, especially gold, on exchanges is a very complex and costly process, because trading in such goods has a number of features: significant volatility, which characterizes the frequent changes in market prices and revenues that can be obtained over time, and a wide range of prices during the day make the product unstable and sometimes unpredictable. It follows that trading in this commodity is a technically complex procedure that requires the necessary training and orientation because if you follow the trading schedule, it is possible to determine turning points and predict market reversal and this is what traders do when monitoring the accumulation of gold in sufficient quantities.

On the example of gold we can trace the efficiency of investing in this precious metal in comparison with stocks, bonds and commodities (Fig. 7).

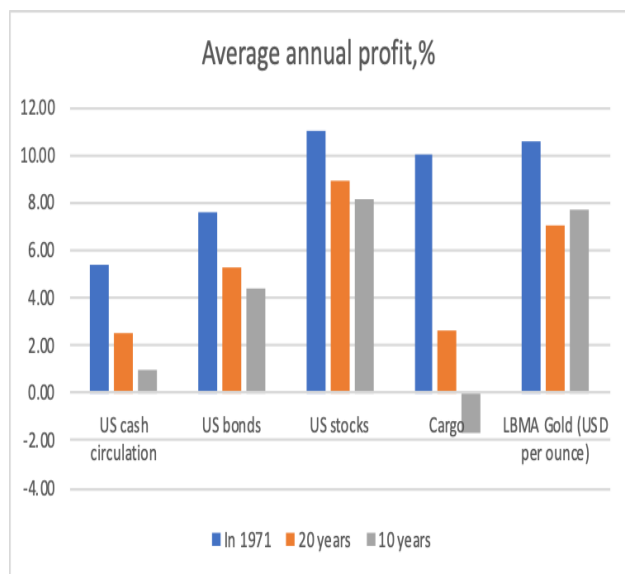


Fig. 7. Long-term efficiency of gold in comparison with other financial assets.

Source: based on [14]

5. Directions of development of the precious metals market in Ukraine

Many scientists say that the market for precious metals in Ukraine is still being formed, although many decades have passed since its inception. However, if we take the time of Ukraine's independence, the beginning of the count is considered to be December 2, 1991, when the Verkhovna Rada of Ukraine adopted the Resolution "On the creation of a stock of precious metals and stones in Ukraine" [15].

The precious metals market is one of the main factors in the efficient functioning of the national economy. In our country, its main function is the accumulation of precious metals in the state register, which makes it possible to carry out operations on the world market of precious metals, which is really necessary in the period of globalization and European integration.

The market of bank metals in Ukraine is more of a cash nature. Using direct and indirect methods in Ukraine influences the regulation of the precious metals market.

In recent years, many Ukrainian banks have already gained some experience in conducting operations in the banking metals market. But the level of its development in comparison with the world metal market is still insufficient. The development of the domestic market of banking metals is constrained not only by objective (insignificant socio-economic level of well-being of potential market participants), but also by subjective factors. These include insufficient practice of using bank metals, in particular:

collateral, obtaining loans, placing deposits, insignificant level of infrastructure development of the Ukrainian market of bank metals.

As for the extraction of precious metals, Ukraine also has its own deposits of silver and gold, palladium has not yet been explored. According to various estimates, the gold content in Ukrainian deposits varies greatly. The most promising today is the Muzhiyivske deposit. According to preliminary data, gold reserves there are more than 50 tons.

Let's name the main features of the road map of development of the national industry of precious metals:

1. The development potential of the precious metals industry is assessed taking into account existing deposits and those that are just being developed.

2. Restoration and improvement of professional training of specialists involved in the precious metals industry, which provide extraction, enrichment, quality assessment of precious metals.

3. Improving the regulatory framework that ensures the circulation of precious metals.

4. Strict state control over the quality and branding of precious products and the formation of a single body that will control these processes.

5. Development of a strategy for the reorientation of the raw materials industry to trade in semi-finished and finished products.

6. Formation of a positive image of our country in the world market, expansion of publicity and publicity of the information illustrating development of the national industry of precious metals.

6. Conclusions

Precious metals are important components of investment portfolios for both individual and institutional investors due to their physical and chemical properties, which allow them to play the role of a reliable hedging tool for long-term prospects. Regarding the effectiveness of precious metals as investment instruments, they should be invested not only for hedging, but also in periods when there are high risks to profit. At the same time, the impact of economic and political situations, financial instability on the profitability of precious metals should be taken into account.

Analysis of price trends in the precious metals market has shown that price fluctuations are different for each metal, they are formed under the influence of supply and demand and market conditions in general. It is important that supply and demand react differently to price fluctuations. Central banks and stock exchanges are active participants in the precious metals market. The process of trading metals on the stock exchange is a complex and multifactorial process, each participant has its own functions, and traders must have certain knowledge in order to make forecasts of market conditions.

As for the precious metals industry in Ukraine, it is only in its infancy. Taking into account the growth of global challenges, instability within the country, to stabilize the national market of precious metals methods can be as follows: development of new technical and technological capacity, creation of state regulatory strategies and institutions that will control the regulation of precious metals in the country; increasing state test control over the misuse and storage of precious metals; creating a transparent market and preventing the use of shadow schemes.

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Organizational determinants of creating and developing energy clusters in Poland

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Abstract: *The subject of the article is organizational conditions of creating and developing energy clusters in Poland. The aim of energy clusters is the development of distributed energy. They are used to improve local energy security in a way that ensures economic efficiency, as well as in an environmentally friendly way by providing optimal organizational, legal and financial conditions. Energy clusters also allow the use of local resources and domestic energy potential. The effectiveness of energy clusters depends on the rational and effective use of potential, i.e. locally available energy resources, renewable energy sources, innovation, entrepreneurship in the area of manufacturing, industry, distribution, as well as management of energy consumption. The aim of the article is to analyze the formal conditions of clusters, in particular the essence of their existence, the tasks that the cluster performs and the role of key cluster participants. As a result of this paper the author shows the process of creation and functioning of a energy cluster.*

KEYWORDS: DISSOLVED ENERGY, ENERGY CLUSTERS, ENVIRONMENT, RENEWABLE ENERGY SOURCES.

1. Introduction

The energy market in Poland is gradually evolving towards the promotion and intensive development of civic energy translating into various regional and local initiatives and activities [1]. One of the visible trends of the global economy, which enables effective management of raw materials and local energy potential, is the development of distributed energy. Forecasts show that these sources can be an important formula for supplementing energy supply in less urbanized areas. The place for the development of these sources are energy clusters. They give the opportunity to build new areas of activity for local entrepreneurs, as well as to accelerate economic growth in the areas covered by the cluster. Thanks to the cooperation of various entities in the energy cluster there is a platform for creating new areas of profits for its participants. The Strategy for Responsible Development developed by the Polish government as one of the main development challenges of Poland indicates: ensuring stable and optimally adapted to the needs of consumers energy supply [2].

Therefore, the reliability of energy supply resulting from the organization of clusters is important for the pace of economic and social development of energy and investment neglected areas. Nevertheless, technical coordination between the generation, supply and use of electricity by businesses, the public sector and households is also important [3].

The aim of the article is to show how the energy clusters function in Poland. The author focuses on the definition of the energy cluster, the purpose of its existence, as well as the tasks that are carried out by the energy clusters and the role of key participants in the energy cluster. In the last part of the article the author focuses on the process of formation and operation of energy clusters in Poland.

2. Preconditions and means for resolving the problem

In Poland, the Centralized National Power System is particularly vulnerable to increasingly frequent extreme weather events and to the large extent of the consequences of failures when they occur [4]. In turn, droughts and hot weather, resulting in low water levels in rivers and its elevated temperature, reduce efficiency and consequently limit the power and amount of energy produced in traditional power plants. It is important to remember that water abstraction from rivers or lake complexes for cooling of open-cycle coal units currently accounts for 70% of the total water abstraction in Poland [5]. Thus, the high variability of precipitation and the increase in non-stationary flows can cause disruptions in the operation of power plants, felt nationwide [6].

The state of Poland's electricity networks is debatable, and the effects of insufficient investment are more noticeable in less urbanized areas. Today, the Polish countryside is heavily polluted by exhaust fumes from household boilers and stoves, untreated sewage, and improperly managed waste [7]. It is estimated that in areas with high dispersion of energy consumers, the frequency of

power outages due to failures can be several times higher than in cities [8]. The same applies to the quality parameters of electricity supply, such as voltage or phase symmetry [9]. Thus, improving the availability of energy and its quality is the basis for activities that reduce barriers to local development.

3. Solution of the examined problem

Energy clusters can turn these nuisances into sources of energy and even profit. The aforementioned Strategy for Responsible Development indicates the values resulting from choosing such - the right path. It requires stimulation of innovation, creativity, development of engineering and scientific potential in Poland and development of Polish technical solutions. This will form the basis for new products offered on the domestic market and globally.

The solution to the problem may be energy clusters, which are in line with and even ahead of the objectives set by the European Union for the coming years. They were included in a package of directives and regulations titled "Clean energy for all Europeans, or how to unleash Europe's growth potential", also known as the "Winter Package", which begins a new chapter in building the European economy after 2020.

Energy clusters are a new concept, it was introduced into the Polish legal order by the Act of 22 June 2016 amending the Act on renewable energy sources and some other acts [10]. Formally, an energy cluster is defined as a civil law agreement, i.e. an agreement concluded by the participants. The agreement may be concluded by natural persons, legal entities, scientific units, research institutes, as well as local government units. Its subject is the generation and balancing of demand, distribution, energy trading (including from renewable sources), or individual elements selected by the cluster members. The activity of the cluster is located within the distribution network with rated voltage lower than 110 kV. The area of cluster activity should not exceed the borders of the economic area, which in Poland is usually the county. The energy cluster is represented by a coordinator. This is any member of the energy cluster or a specially established cooperative, association, foundation, etc. [11].

In accordance with the above definition, as an energy cluster can be considered an agreement between locally operating entities dealing with the production, consumption, storage and sale of: electricity, heat, cold and electricity in transport (fuels). The cluster formula is flexible enough to allow participants to build an individual business model of cluster operations and choose the optimal legal form of its activities. Cluster members do not have to give up their current activities, but through cooperation - wherever it brings benefits to them and other cluster participants - they generate added value for the local community. Joining or leaving the cluster may or may not have a significant impact on the activities of other members. Table 1 presents the role of key members of energy clusters.

Table 1. The role of key participants in the energy cluster

Cluster Participant	The role of a cluster participant
Power Generators	They may be the initiators of the cluster, interested in its development due to the sale of energy and the possibility of implementing new investments in technical infrastructure, including in particular energy production.
Energy cluster coordinator	It can be one of the members of the cluster or an entity appointed specifically to perform this function within the cluster. It conducts current affairs of the cluster, administrative services, provides legal and tax services, represents the cluster externally.
Final recipients	Related to the cluster because of the perspective and opportunity to optimize supply costs and improve energy quality.
Local Self-Government Units	They are important stakeholders in the cluster. They may be the initiators of its creation because of the prospect and possibility of optimizing supply costs and improving energy quality, as well as the possibility of being an indirect beneficiary of increased opportunities to obtain funding through the cluster.
Companies	Business units (small, medium and large enterprises) related to with the use of energy - production, trade and services. These enterprises, depending on their size, have different qualitative and quantitative needs that must be provided in whole or in part by the energy cluster.
Public transport companies	Their membership in the cluster is aimed at securing access to low-emission fuels (biofuels) or energy from renewable sources or from waste sources from industry (development of low-emission transport - electromobility).

Source: Own study based on [12].

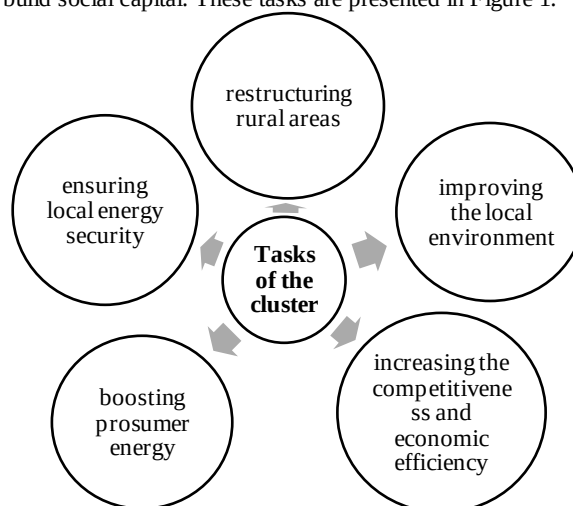
Considering the purpose of the existence of clusters, it should be pointed out that the goal set by the Ministry of Energy for cluster market participants is to identify and implement such business models that will be able to maintain and compete in the market in an effective manner, also without financial support in the long term. Thus, the development of energy clusters enforces the development of rules for the interaction of equal entities in the cluster [13]. An important role in this case is also played by the cooperation of energy producers with network operators. In turn, the objectives of creating and developing energy clusters in Poland should be considered [14]:

- Creating self-balancing areas of the electricity grid,
- Development of renewable energy,
- Ensuring reliability of supply and low prices of energy and distribution services in the area,
- Improving local energy security by creating energy self-sufficient regions - increasing energy efficiency,
- Ensuring better conditions for local entrepreneurs, attracting new investors,
- Supporting low-emission economy, reducing negative impact on environment,

- Modernization of rural areas and supporting development of municipalities,
- Diversification of income in rural areas,
- Creation of new jobs,
- Reduction of electricity costs borne by local governments,
- Increase in innovation - cooperation with scientific institutions and R&D,
- Increase in awareness of the local community regarding the production and consumption of electricity and heat.

Another important issue considering the purpose of clusters is its addressees. The energy cluster is represented by a coordinator, which is a cooperative, association, foundation, or any member of the energy cluster [15]. The energy cluster is addressed to a very wide range of stakeholders and customers whose activities or needs are related to electricity and/or heat [16]. It is a platform for cooperation between local government units, the scientific community, entrepreneurs and their organizations, and all institutions and entities that declare themselves involved in the implementation of the objectives set by the cluster.

Having indicated the purpose of existence of clusters and its addressees, it is worthwhile to outline the tasks that are undertaken by the energy cluster. The tasks of energy clusters are to ensure local energy security, improve the local environment, and increase competitiveness and economic efficiency of the local economy. Cooperation within clusters can also contribute to the restructuring of rural areas, prosumer energy stimulation and further development. Through the development of these initiatives, it will be possible to achieve an increase in innovation and build social capital. These tasks are presented in Figure 1.

**Fig. 1** Tasks of the cluster

Source: Own study.

4. Results and discussion

Energy clusters primarily pursue individual goals of their members while being able to plan and implement local goals. Broader, regional or national goals can be achieved through economies of scale. However, attachment of cluster members to tasks of national character has a limited range, which results from the strictly bottom-up character of cluster initiatives. Based on the analysis, it is possible to detail the various stages of energy cluster formation, which are presented in Figure 2.

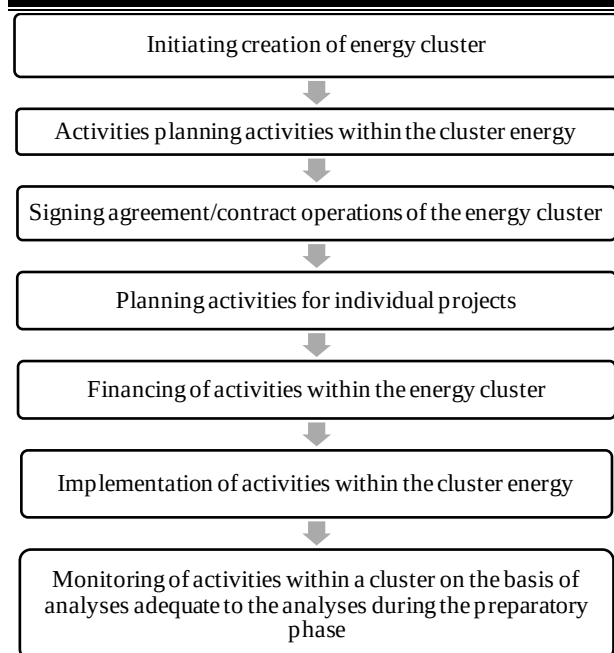


Fig. 2 Diagram showing the process of creation and functioning of a energy cluster

Source: Own study based on [5].

Cluster participants can achieve many potential benefits through cluster cooperation. Firstly, it is obtaining a lower cost of energy and obtaining funding for planned investments. Secondly, participation in energy auctions dedicated to clusters. Cluster participants can also count on solving local problems related to, among others, low emissions, development of new energy sources (dispersed energy), raising residents' awareness of environmental attitudes, maintaining the status of spa municipalities or creating the image of a green municipality, creating new jobs or development of underdeveloped areas.

5. Conclusion

The development of distributed generation is seen as an opportunity to increase energy security through greater diversification of fuel and energy production. Distributed sources also provide greater possibilities for production control, and their location close to consumers and cooperation with networks with rated voltage below 110 kV can significantly reduce the construction of costly high-voltage networks in the long term.

The idea of energy clusters, strongly promoted in recent months, has started to be put into practice. There are already several dozen such structures in Poland, with new ones joining every week. The models of functioning are different and so are the organizations forming them. Energy clusters have a chance to become an important element of Polish economy both on regional and national level, especially supporting development of less urbanized areas. Rural or urban-rural municipalities could become attractive areas for investment on condition that certain investments can be included in the energy cluster initiative.

6. References

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Factors affecting the cost of electricity from geothermal power plants

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Abstract: This article analyses the factors affecting the cost of electricity from geothermal power plants. Geothermal power is a capital-intensive technology and the installation costs are highly site sensitive. The costs of geothermal electricity are influenced by the thermal properties of the reservoir, the costs of site exploration and wells drilling, the number and depth of the wells, the power plant type. The choice of the power plant type depends on the properties of the geothermal resource, its temperature, quantity and quality. Being site- and technology-dependent, the installation costs for geothermal power may be as low as 2000 US\$/kW and as high as 7000 US\$/kW, with the global weighted average at 4000 US\$/kW. This wide range of installation costs translates into levelized cost of electricity (LCOE) between 40 US\$/MWh for upgrade and expansion projects and 170 US\$/MWh for greenfield projects. The global weighted average LCOE is estimated at 70 US\$/MWh. Further costs reductions may be accomplished through the research and development of more innovative and low-cost techniques for site exploration and drilling as well as with advanced exploitation methods for geothermal reservoirs.

Keywords: GEOTHERMAL POWER PLANT, LEVELIZED COST OF ELECTRICITY, GEOTHERMAL RESERVOIR

1. Introduction

Geothermal energy is a renewable source of energy utilized for electricity generation and thermal energy supply. For electricity generation, medium- and high-temperature geothermal resources are necessary while the most-abundant low-temperature resources are used for the heating of buildings or agricultural and fish farms. Geothermal power plants rely on well-developed technologies for the utilization of conventional geothermal resources such as dry steam, flash plants (single, double and triple), binary plants, combined-cycle and hybrid plants. However, as high-quality geothermal resources become fully exploited, alternative deeper geothermal resources could be accessed through the research and development of advanced geothermal systems. The total global installed geothermal power capacity has been steadily increasing in the last decade: 10.9 GW in 2010, 12.3 GW in 2015, 16.0 GW in 2020 and it is expected to reach 20 GW by 2025 [1]. The technical potential for geothermal power is estimated at 200 GW (IPCC, 2011). This potential could be realized in the future with the use of advanced reservoir exploration and drilling methods as well as with the development of advanced geothermal technologies.

The global generated electricity from geothermal power plants was 96 TWh in 2020, which amounts to 0.35% of the global electricity generation. Table 1 gives the full list of all the countries generating electricity from geothermal resources. For comparison, the total global wind power capacity of 622.7 GW generated 1429.6 TWh of electricity while the total global solar power capacity of 586.4 GW generated 724.1 GWh of electricity in 2020 [2]. Although solar and wind energy are renewable sources with the highest annual installation rates, the advantage of geothermal energy is its year-long availability, with less degree of variability and intermittence. The equivalent number of full-load hours is 5938 for geothermal, 2295 for wind and 1235 for solar energy, over a one-year-time with 8760 hours.

Geothermal energy offers vast possibilities for clean and sustainable energy generation and supply, at acceptable costs and low emissions of greenhouse gases. Cost-wise, geothermal power plants are becoming increasingly competitive, and the installation costs are expected to continue to drop in the following decades. The average investment costs for geothermal power plants are approximately 4000 US\$/kW per unit of installed capacity, whereas the exact costs are highly site-sensitive and also depend on the technology and project type [3]. The geothermal cost range is generally between 2000 and 6000 US\$/kW, with binary cycles that are generally more expensive than direct dry steam and flash steam units. The weighted average levelized cost of electricity (LCOE) for geothermal power plants was 73 US\$/MWh, which is slightly higher than the LCOEs of most other renewable energy sources: 47 US\$/MWh for hydropower, 53 US\$/MWh for onshore wind, 60 US\$/MWh for biomass, 68 US\$/MWh for solar photovoltaics,

115 US\$/MWh for offshore wind and 182 US\$/MWh for solar concentrators [4]. Emission-wise, geothermal power plant operate with specific CO₂ emissions in the range between 20 and 57 kg/MWh, comparable to other renewable energy sources. The carbon footprint from solar PV power is between 29 and 80 kg/MWh from wind power it is between 8 and 20 kg/MWh while large hydro power plants achieve the lowest CO₂ emissions – in the range between 3 and 7 kg/MWh [5].

Beside high resource availability and low-cost/low-emission electricity generation, geothermal power presents several more advantages. Geothermal energy is not affected by the rising energy prices and the gradual depletion of fossil fuels, it contributes reducing a country's dependence on import fossil fuels, it poses no risks to the public health or to the environment, it can be operated both for base-load or peak-load electricity generation, and it achieves high capacity factors at flexible and reliable operation.

Table 1: Net installed capacity and generated electricity from geothermal power plants by country in 2020 [1]

Country	Net installed capacity, MW	Generated electricity, GWh
USA	3700	18 366
Indonesia	2289	15 315
Philippines	1918	9 893
Turkey	1549	8 168
Kenya	1193	9 930
New Zealand	1064	7 728
Mexico	1006	5 375
Italy	916	6 100
Iceland	755	6 010
Japan	550	2 410
Costa Rica	262	1 559
El Salvador	204	1 442
Nicaragua	159	492
Russia	82	441
Guatemala	52	237
Chile	48	400
Germany	43	165
Honduras	35	297
China	35	175
Portugal	33	216
France	17	136
Croatia	16.5	76
Papua New Guinea	11	97
Ethiopia	7.3	58
Hungary	3	5.3
Austria	1.3	2.2
Belgium	0.8	2.0
Australia	0.6	1.7
Taiwan	0.3	2.6
TOTAL	15 950	95 100

2. Geothermal power technologies

Ranked by global market share, the most utilized geothermal power technologies are: 1) flash steam: 58%, 2) dry steam: 26% and 3) binary cycle: 15%. *Flash steam units* use high-pressure and high temperature ($>180\text{ }^{\circ}\text{C}$) hot water that boils into steam inside high- and low-pressure separator tanks. The steam expands in the turbine and the mechanical work drives the electric generator. *Dry steam units* use exclusively dry geothermal steam with temperatures higher than $150\text{ }^{\circ}\text{C}$, which is directly expanded in the turbine. Condensed water is pumped back into the geothermal reservoir by means of injection wells. *Binary cycle units* operate with geothermal temperatures between $60\text{ }^{\circ}\text{C}$ and $200\text{ }^{\circ}\text{C}$ in double loop configuration. The geothermal fluid flows inside the primary loop while the working fluid flows in the secondary loop. The primary loop supplies heat to the secondary loop, which is in fact an Organic Rankine Cycle (ORC). The selection of the working fluid depends on the geothermal temperature and the cycle configuration [6-7]. Most recently, *hybrid cycle units* are being tested at the prototype stage. These geothermal power plants are going to combine low-temperature ORC cycle to utilize the heat that would otherwise be wasted from flash steam or dry steam units. Using two combined cycles ensures higher thermal efficiency than in single cycles.

Advanced geothermal power technologies are currently being researched and developed to take advantage from resources that would otherwise be wasted. These technologies encompass: 1) low-temperature bottoming cycle, 2) cogeneration, 3) co-production and 4) supercritical geothermal resources. In *low temperature bottoming cycles* geothermal flash units are retrofitted with low-temperature bottoming cycles. Flash steam configurations are generally employed when dealing with high-enthalpy geothermal resources. In a flash steam unit plant, the steam exiting the turbine is reinjected into the geothermal reservoir. However, the temperature of this steam is suitable for additional power generation in a binary cycle turbine, which would increase the overall net electricity generation. In *cogeneration*, geothermal power plants are coupled to district heating or agricultural/farming applications for the use of low-temperature heat (less than $100\text{ }^{\circ}\text{C}$) that would be otherwise wasted in cooling towers. In *co-production*, hybrid power plants use geothermal energy combined to different heat sources such as concentrating solar, biomass or industrial waste heat. This additional heat would be added to the geothermal fluid increasing the temperature and the output of the electricity generating unit. For example, the *Stillwater power plant* is a triple hybrid geothermal and solar CSP/PV unit in Nevada, USA. It consists of a 33.1 MW geothermal power plant, a 26.4 MW solar PV power plant, and a 2 MW solar CSP thermal power plant. This triple hybrid power plant combines the continuous capacity of a medium enthalpy geothermal binary cycle with solar PV and solar thermal to generate 241 GWh of electricity annually. In Tuscany, Italy, a hybrid biomass-geothermal power plant uses biomass heat to increase the temperature of the geothermal brine and thus the thermal efficiency of the power plant. The 20 MW geothermal power plant uses the additional 6 MW of biomass capacity to boost electricity production and cycle efficiency by rising the geothermal steam temperature from $150\text{ }^{\circ}\text{C}$ to $370\text{ }^{\circ}\text{C}$ before the turbine inlet.



Fig. 1. Aerial view of the Stillwater triple hybrid geothermal-solar power plant, Nevada, USA.

Supercritical geothermal resources are high-temperature resources where the geothermal fluid is in the supercritical state, above $374\text{ }^{\circ}\text{C}$ and 221 bar for water. These geothermal resources are currently the subject of ongoing research and are expected to enter commercial operation in the future. Compared to conventional geothermal resources, supercritical resources are capable of achieving higher well productivities, better cycle efficiency and more electricity generation [7]. The Iceland Deep Drilling Project found a high-temperature well capable of producing superheated steam at $450\text{ }^{\circ}\text{C}$, at a rate of $0.7\text{ m}^3/\text{s}$, sufficient for an estimated 45 MW of electricity generation. This exploratory well found a magma reservoir at 2100 meters, after it was initially planned to drill down to hot rock below 4000 meters. The aim was to improve the cost-effectiveness of geothermal power. The second high-temperature well, also drilled in Iceland, found a supercritical geothermal fluid with a temperature of $427\text{ }^{\circ}\text{C}$ and a pressure of 340 bar, at a final depth of 4,659 meters. Supercritical wells can exploit the steam directly from the reservoir or the reverse approach could also be used. This would mean injecting the fluid into the high-temperature reservoir to enhance the performance of the existing conventional geothermal power plant.

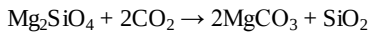
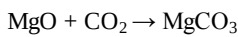
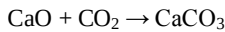
A substantial fraction of the geothermal potential is located at drilling depths greater than for typical geothermal projects, in the excess of 3000 meters' depth. The exploitation of geothermal resources depends on the presence of permeable aquifers, which allow for the drawing of hot water through them. At greater depths, the soil becomes less porous and the water flow is reduced. Research projects are being carried out to overcome this limitation. Production and injection wells can be connected through artificial fractures created by the injection of water and a small amount of chemicals at high pressure to stimulate formation of fractures in the hot bedrock, a process known as hydraulic fracturing. After supplying heat to the geothermal binary cycle, the geothermal brine is reinjected into the reservoir to keep the pressure and production stable. This also prevents the emission of CO_2 and other harmful gases into the atmosphere during the service life of the geothermal power plant.

3. Barriers to geothermal development

The principal barriers to the development of geothermal power are financial, social, environmental and administrative. Geothermal power projects are capital-intensive, especially due to the cost of exploration drilling, for which it can be difficult to obtain long-term bank loans. Geothermal exploration is considered a high risk phase, which could potentially result in failure, and developers may have to obtain some form of prior public funding. This risk derives from the fact that capital is required before the resource exploitability is confirmed, and before the project profitability can be assessed. The risk to private developers can be mitigated in a number of different ways. For example, risk-sharing between private developers and public companies may be a possible solution when both parties are interested in exploiting the geothermal resource [4]. Geothermal resource information such as seismic and drilling data may be made available by local authorities to attract more interest from private developers and accelerate the realization of geothermal projects.

Other barriers include environmental concerns, social disapproval and administrative constraints. For instance, a geothermal project may be delayed or even cancelled after discussions and negotiations with local groups, land owners and authorities, which may be concerned about the social and environmental impact of the project. Administrative barriers include unwanted project delays due to the issuance of exploration licenses and drilling permit. Furthermore, different countries might have different procedures and regulations for assessing the environmental and social impact, which is mandatory in most cases. Local authorities and state governments should establish transparent regulations and effective procedures in order to attract more project applications and avoid unwanted project delays.

As far as it concerns the environmental impact, the geothermal fluid drawn from the deep reservoir typically contains a mixture of gases, carbon dioxide (CO₂), hydrogen sulfide (H₂S), methane (CH₄), ammonia (NH₃), and radon (Rn). These gases contribute to the global greenhouse effect, acid rain formation and noxious smells [8]. Geothermal power plants generate electricity at a total life-cycle emission of 45 kg_{CO2}/MWh, on average. Geothermal power plants with high levels of acid compounds and volatile chemicals in the geothermal fluid are usually equipped with emission-control systems and use fluid reinjection into the reservoir. For example, the CarbFix project captures and stores 200 tons of CO₂ per year into the subsurface at the site of the Hellisheiði geothermal power plant in Iceland. The CarbFix project is capable of capturing 68% of the H₂S and 34% of the CO₂ produced in the geothermal power plant. The CO₂ is captured as a dissolved phase in water and injected to a depth of 750 meters underground into the basaltic rock, where it reacts with the host rock to form stable carbonate minerals, thus providing for safe, long-term storage of the captured CO₂. Research results showed that 95% of the injected CO₂ was permanently solidified into calcite within 2 years, using 25 tonnes of water per tonne of injected CO₂. The carbonated water is injected into the subsurface where carbon-fixing reactions with calcium oxide (CaO), magnesium oxide (MgO) and silicate minerals (Mg₂SiO₄) solidify the carbon dioxide (CO₂):



The cost of drilling and injecting carbonated water at high pressures into the basaltic rock was estimated at 25 US\$/ton. At the downside, injection of carbonated water requires substantial amounts of water and the presence of carbon-fixing rocks, which may not be available in all localities. Furthermore, the injection of pressurized water into the subsurface may induce seismic activity in the area. Another example is the Kizildere geothermal power plant in Turkey, where the carbon dioxide from the geothermal fluid is processed into dry ice. The annual dry ice production in Kizildere is 80,000 tons while the hot geothermal fluid is used to heat 50 acres of agricultural greenhouse spaces and 2,500 households before being reinjected into the geothermal reservoir.

Beside containing dissolved acid gases, the hot geothermal fluid sources may hold trace amounts of toxic chemicals such as mercury (Hg), boron (B), arsenic (As) and antimony (Sb) [8]. If released into the atmosphere, these chemicals can cause damage to ecosystems. Generally, the environmental impact of geothermal power is much lower than that of conventional fossil fuel power. For instance, the land requirement of geothermal units per unit of generated electricity is 400 m²/GWh while that of coal power plants is five times as much (1500 m²/GWh). The freshwater use of geothermal units is 20 m³/GWh while that of fossil fuel power plants is more than fifty times as much (1000 m³/GWh).

4. The cost of geothermal electricity

On the one hand, geothermal power projects are capital intensive but, on the other hand, they have low maintenance and operating costs. The capital investments comprise the costs of project development, the resource exploration and assessment, the drilling of exploratory boreholes, the drilling and construction of production and injection wells, the construction of collection and disposal systems for the geothermal fluid, the construction of the power plant infrastructure and grid connection costs. Furthermore, the costs of geothermal projects are site- and technology-sensitive, meaning that they depend largely on the power plant type, the well productivity and other characteristics of the geothermal field.

The specific investment costs per unit of installed geothermal capacity are typically in the range between 2000 US\$/kW and 5000 US\$/kW, for most projects but may be as high as 7000 US\$/kW for

advanced geothermal systems and binary cycles. The lower end of the cost range is for retrofit and upgrade of existing geothermal power plants while the upper end of the cost range is for more challenging site conditions and geothermal reservoir properties. Generally, installation costs for binary cycle geothermal power plants are higher than those for direct steam and flash steam geothermal power plants, as shown in Figure 2. For instance, the first geothermal power plant in Croatia, a 13.5 MW binary cycle, was commissioned in early 2019 at a total investment cost of €44 million, corresponding to specific costs of 3260 €/kW (4000 US\$/kW). The generated electricity is 82 GWh per year, at average capacity factor of 70%, equivalent of 6100 full load hours [9-10].

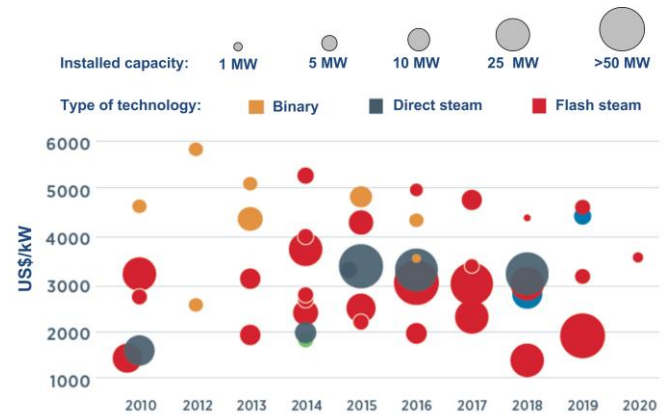


Fig. 2. Installation costs for geothermal energy by type of technology and project size, 2010-2020 [3].

Geothermal energy installation costs are within the costs range of other renewable energy sources, as shown in Figure 3. For instance, the average installation costs of geothermal energy are higher than those for onshore wind (1070 US\$/kW), rooftop solar PV (1646 US\$/kW) and utility solar PV (1130 US\$/kW), hydro power (1704 US\$/kW) and biomass (2140 US\$/kW), comparable to the costs of offshore wind (4100 US\$/kW) and lower than the costs of solar CSP (5770 US\$/kW) [4]. Due to the ongoing research and further development of geothermal technologies and system components, geothermal installation costs are expected to drop by 30% in the following decades.

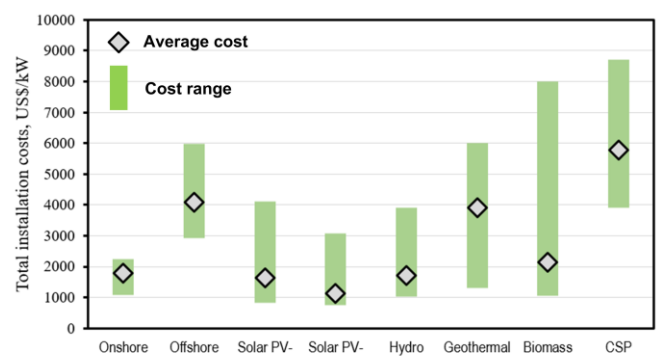


Fig. 3. Comparison of installation costs for geothermal power and other renewable sources for electricity generation, 2020.

In the last decade, the levelized cost of electricity (LCOE) for geothermal power varied between 40 US\$/MWh for second-stage upgrade and expansion projects to as high as 150 US\$/MWh for greenfield projects in remote areas. In the overall LCOE, operation and maintenance (O&M) costs are estimated between 10 and 20 US\$/MWh. The global weighted-average LCOE increased from 50 US\$/MWh in 2010 to around 70 US\$/MWh in 2020, although annual weighted-averages are quite variable, as shown in Figure 4.

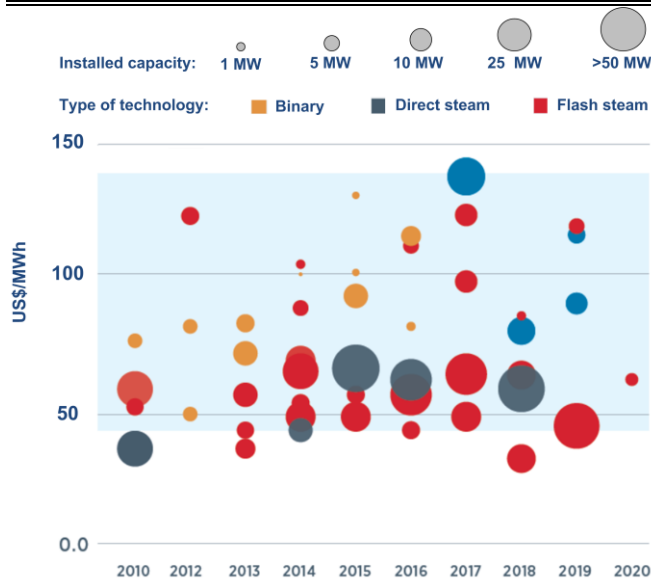


Fig. 4. Levelized cost of electricity (LCOE) for geothermal energy by type of technology and project size, 2010-2020 [3].

Although total installation costs of geothermal power are higher than those for other renewable energy sources, the high capacity factors of geothermal power plants reduce the specific costs of electricity generation. For comparison, the average levelized cost of electricity (LCOE) for geothermal electricity is 73 US\$/MWh while those for the other renewable sources are: 67 US\$/MWh for onshore wind and 117 US\$/MWh for offshore wind, 105 US\$/MWh for utility PV and 138 US\$/MWh for rooftop PV, 47 US\$/MWh for hydro power, 66 US\$/MWh for biomass, 182 US\$/MWh for solar CSP [3], as shown in Figure 5.

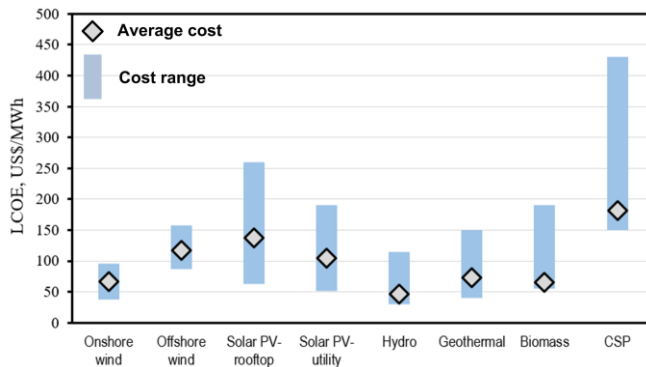


Fig. 5. Comparison of LCOEs for geothermal power and other renewable sources, 2020.

Generally, the costs of geothermal electricity are affected by a number of different categories such as the thermal properties of the reservoir, site exploration and wells drilling, the number and depth of the wells, the power plant type, the construction of the necessary infrastructure. The estimated cost breakdown for a flash steam power plant in the EU, with total installation costs of approximately 3000 US\$/kW is as follows: 1) the costs of the power plant infrastructure amount to 56% of the total installation costs, 2) exploratory wells, production and injection wells account for 21% of the total costs, 3) project management and engineering supervision accounts for 12% of the total costs, 4) connection to the local grid costs 7% and 5) the costs of insurance are 4%. The cost breakdown for a binary cycle power plant in the EU, with total installation costs of 4000 US\$/kW is similar to that of the flash steam power plant: 1) the power plant infrastructure costs 55%, 2)

the costs of exploratory wells, production and injection wells are 30%, 3) project management and engineering supervision costs are 7%, 4) grid connection costs 5% and 5) the insurance costs are 3%.

5. Conclusions

Geothermal projects are capital-intensive, especially because of the high costs of exploratory wells and geothermal resources assessment, for which it can be difficult to collect the necessary funding. The risk to private developers can be mitigated with risk-sharing schemes between them and public companies. Geothermal resource information such as seismic history and drilling data may be made available by local and state authorities. Other barriers include administrative constraints, environmental concerns and social disapproval. For instance, a geothermal project may be delayed after discussions with local groups, land owners and authorities, which may be concerned about the social and environmental impact of the project. Administrative barriers include unwanted project delays due to the issuance of exploration licenses and drilling permits. Local authorities should establish transparent regulations and effective procedures in order to attract more project applications. The interest in the development of geothermal projects could be accelerated if these barriers are removed or at least mitigated, and effective business procedures are established.

The total global geothermal capacity is expected to continue growing in the years to come. The global generated electricity from geothermal energy was 96 TWh in 2020, which amounts to 0.35% of the global electricity generation. However, the technical potential of geothermal energy is much higher, capable of supplying up to 5% of the global electricity demand. As of 2020, the average installation costs in geothermal power plants are approximately 4000 US\$/kW while the levelized cost of electricity generation (LCOE) is 73 US\$/MWh, which is comparable or even better than the costs for other renewable energy sources.

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An Integrated Approach toward a sustainable transport sector using EnergyPLAN model: case of Albania

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Abstract: In Albania, prior to the 1990's, the industrial sector was the leading energy consumption sector but actually, the main cause of pollution especially in urban areas, carcinogenic, respiratory and heart diseases come from road transport sector. The environmental situation in Albania after 30 years has undergone major changes due to factors that directly or indirectly influence the degree of its pollution which still remain an unresolved issue. Tirana's fleet vehicle shares around 35% of the total car fleet registered in Albania. DCI vehicles constitute approximately 71% and the rest petrol powered engine, while the number of EV and other friendly fuel sources is almost zero. The proposed work aims at developing different transport scenarios contributing to the mitigation of GHG in Albania. Using EnergyPLAN model, 3 different scenarios are proposed, considering both most prominent national documents firstly: "Albanian Energy Strategy 2018-2030" which requires a reduction level of CO₂ by 11.5% in 2030 referring to 2006 to attain a RES share of 42% to the TPES and secondly to create a sustainable transport sector as foreseen in "National Sector Strategy for Transport 2016-2020". This modelling framework analyse the actual transport situation and can address some beneficial values and solution which can be used from policy makers in the country to better assess the potential for a sustainable, environmentally friendly and cost-effective transport sector based on RES.

KEYWORDS: ENERGYPLAN, CO₂, GHG,

1. INTRODUCTION

Transport sector in Albania has traditionally been and still continue heavily reliant on oil products which accounted for 100% of transport energy demand in 2020. Consequently, special support should be given to candidate countries in creating clear transport policies and programs for a sustainable transport sector based on green technologies. Transport is the largest source with the fastest growing contribution of CO₂ fossil fuel-based emissions emitting around 7GtCO₂ in 2020 and 8,5 GtCO₂ in 2019 before pandemic.

The idea for a clean, sustainable, flexible, and environmentally friendly energy system is quite impossible and unimaginable without the promotion of RES as it is considered the backbone of the global energy transition [1,2,3]. Encouraging of renewable-sourced energy systems is set to become the dominant energy carrier in the global energy system and will play a major role in the process of decarbonisation of energy systems including transport sector especially [4]. Hence, promoting healthy, sustainable transportation options prevents the negative effects of current transportation models on human health, such as those caused by air pollution and physical inactivity. Global warming and the rise of diseases in the human body caused by environmental pollution pose a major global risk to today's society.

Under IRENA's Transforming Energy Scenario a combination of energy efficiency improvements, modal shifts, electrification, and the use of alternative fuels can reduce the transport sector's energy-related CO₂ up to 1.8 Gt per year in 2050, compared to an increase to 5.4 Gt per year observed in the Planned Energy Scenario. In developed countries, physical inactivity bears a major risk factor for health problems leading to a yearly inactivity cost calculated around €150-300/person.

Rapid growth regarding number of private vehicles, as well as the urban development and densification, combined with a public transport that can't fulfil all mobility needs of the community and lack of infrastructure negatively affect the urban population and force community to cover distances less than 5km per day by using their private vehicles. This situation creates rush hours, high rates of fuel consumption, hence leading to high emission level rates. For several years, Albania has been involved in rapid urban development, which has brought a relatively high impact on the environment and also negatively affecting people both physically and physiologically. Environmental noise, and in particular road traffic noise, remains a major environmental problem affecting the health and well-being of millions of people in Europe. More than 27% of European citizens are exposed to transport noise levels of 55dB or higher, including 15-20% for road traffic noise alone [5].

2. EMISSION STANDARDS FROM ROAD TRANSPORT SECTOR

Environmental pollution caused from the transport sector is one of the main problems in Albania which rank the last country in Balkan region [6,7]. Emission standards for passenger cars (M1 vehicle category) are discussed in the study [7] and starting from the Euro 2 stage, EU regulations introduce different emission limits for diesel and petrol vehicles. Diesel engines have more stringent CO standards but allow higher NO_x emissions. Petrol-powered vehicles were exempted from particulate matter (PM) standards through the Euro IV stage, but vehicles with direct injection engines will be subject to a limit of 0.005 (g/km) for Euro V and Euro VI. From 2011 up to 2020 the emission test is realized from SGS Automotive Albania and from 2021 the service is performed by the responsible own state company.

The procedure of emission test including diesel and petrol vehicles of M1 category is given in the study of [7] and still remains the same in terms of restrictions in the post combustion gases. Traffic-related emissions of fine particles represent one of the main sources of air pollution especially in urban areas [8]. In the study of [7] it is observed that opacity value was extremely high referring to for the vehicles produced before 2002.

Vehicles with ages more than fourteen years have very high opacity level and the most problematic groups that cause high pollution level come from the produced years 1980 up to 2002. Unfortunately, a slight improvement compared to the results in [7-8] is identified, as vehicles of age 11-20 years dominate and considering the fuel quality which remains another unresolved issue for the government (refer graph in figure 5) hinders and further complicates the position of the transport sector in Albania.

3. PURPOSE OF THE STUDY

Recently, more diverse challenges have emerged in society such as climate change, security of energy supply, and economic recession. As a result, the transport sector, especially renewable fuels, is being targeted to disappear these issues. The purpose of this study is to determine the best scenario since the new energy technologies shift from one to another should be more precise, converting from an energy-system that is dependent on imported fossil-fuels to a renewable energy-system can play a significant role in solving these issues [9]. Our hypothesis is that the growth in energy demand and fluctuations of energy systems cause gaps in which the real options towards a sustainable transport sector and may be affected by the application of the new proposed technologies. Detailed energy system analysis and simulation are seen as a success key to identify the affected technologies, the environmental impacts and compared between different scenarios fully in line with the national energy

strategy requirements. According to MIE in Albania greening the transport sector through e-mobility has the potential to positively contribute to the balancing of the power system through peak-load shaving, reducing distribution losses and reducing air pollution. Hence, this work will provide an overall energy strategy aimed at the diversification of the transport sector which should be developed as a cross-sectoral collaborative effort between relevant authorities and both the MIE and Energy Regulatory Authority (ERE) to ensure a coordinated and coherent development pathway for both the energy and transport sector. Such a strategy could also encourage and promote the inland produced biofuels such as biodiesel, bioethanol and bio-methane. Integration of biofuel especially in transport sector should deal with biomass sustainability criteria which will increase the national energy security, decrease dependence from oil imports, improving air quality in urban centres and the most important thing is that will help diversification of the agriculture and rural economies in Albania [10,11].

Under the European Green Deal [12], the Commission committed to present, in 2021, a proposal to apply more stringent air pollutant emissions standards for combustion-engine vehicles through on post Euro 6/VI standards. The European Green Deal is a new growth strategy that will foster the transition to a climate-neutral, resource-efficient and competitive economy and the move towards zero-pollution in Europe [13]. It will also aim to reduce the complexity and compliance costs of the existing Euro 6/VI vehicle emission standards; provide appropriate and up-to-date limits for all air pollutant emissions; and ensure that new vehicles keep their air pollutant emissions under control throughout their entire lifetime and in all conditions of use [13]. On the European Green Deal, the Commission's focus will be overhauling our relevant climate and energy legislation to align with the newly proposed target to reduce emissions by at least 55% by 2030, as compared to 1990 levels. The depth and breadth of the work planned across the European Green Deal reflects the systemic nature of the green transition and its importance as a growth strategy. Putting forward a series of measures on smart and sustainable transport, including a revision of the Regulation on the trans-European transport network and of the Directive on intelligent transport systems is very crucial [13].

3.1 BASIC PRINCIPLES OF THE METHOD AND NATIONAL REGULATIONS.

The basic principles of this method the scenarios are created are as follows: The chosen method involves the actual fuel types and the need to introduce other friendly fuels based on inland potential and global trends within transport sectors are the main pillars of the methodology. Such a strategy could also encourage and promote the inland produced biofuels such as biodiesel, bioethanol and bio-methane. This is essential for implementation of the Smart Energy Systems concept, because the fundamental objective of this theory is to take advantage of possible synergies by combining all sectors of the energy system. In this point of view different fuels from different sectors are combined to check the two main goals of the "National Energy Strategy 2018-2030" and "National Sector Strategy for Transport 2016-2020".

- ☞ **Reaching a RES share up to 42% in 2030;**
- ☞ **Decreasing CO₂ emission by 11.5% referring to the 2006 level.**

The present "National Sector Strategy for Transport 2016-2020" has been aligned with the National Strategy for Development and Integration which defines Albania's vision for its national social, democratic and economic development over the period 2015-2020. The strategic priority is to accelerate the integration of Albania's transport system and the establishment of an integrated market comprising the whole transport infrastructure. Despite significant investments especially in improving road infrastructure, the transport sector has yet to become a significant promoter of economic development in Albania.

4 FEATURES OF THE ALBANIAN ENERGY SYSTEM

Having in mind the fact that electricity comes from RES (almost 100% hydro sources), a balanced configuration of the

energy system dominated by fossil fuel powered vehicles (100%), will be preferred by an energy system with opposite fuel portions. This fact, together using technical approach of the current study will help in the selection of the optimal RES configuration in the transport sector. Combining different technologies that support new fuel types in compliance with the main two objectives of the national energy strategy and sector strategic action plan is mandatory. This analysis is very hard and may require the use of technologies that are still in the early stages of development. The total final energy consumption in Albania referring 2018 is 24 TWh (2081ktoe) where the consumptions by different sectors in Albania is given in table 1 [14]. Indeed, the transport sector is by far the biggest consumer of energy sharing 40% of PES in Albania. According to [10] in 2018, Albania's total primary energy supply (TPES) amounted to 2131(ktoe).

Table 1: Distribution of primary energy supply by demand sector, 2018. Source: [15]

Sector	%
Transport	40
Residential	24
Industry	20
Services	10
Other	6

Table 2: Fuels going through Final Energy Consumption in Albania, 2018. Source [1,10]

	%
Crude, NGL and Feedstock	57
Hydro electricity	25
Solid fuels	9
Biomass (Fuelwood)	8
Solar energy	1
NG	Negligible
Derived heat	0

Distribution of energy by fuel type going to the final energy consumption in Albania is given in table 2. Crude oil cover around 57% of the final energy consumption in the country followed by hydroelectricity 25%, biomass as wood fuel type 8%, solid fuel 9% and the rest (1%) comes from solar energy. Albania's electricity demand grew rapidly in 1995- 2000. This was due to demographic, economic and social trends, including rural-to-urban migration, increased use of electricity for space heating and cooling and rising living standards [16].

The Albanian power system is dominated by hydropower, representing more than 95% of the country's installed capacity with a total of 2,506 MW installed. The majority of the installed capacity (1448MW) 58% is owned by the Albanian Power Corporation (KESH) and the rest 42% belongs to the private producers (1058MW) [17] (where the installed capacity of independent producers is 436 MW, while 622 MW belongs to the producers with priority). According to [10] the installed hydropower capacity comprises mainly large hydropower installations (i.e., above 10 MW in size) constituting 1904MW, while small hydropower installations amount to 192MW. The country has a 98MW fossil-fuel thermal power plant representing 4% of the total installed capacity that has not been put into use since its construction in 2011 due to a failure in its cooling system. In January 2019, the MIE issued a tender for a public-private partnership (PPP) for a concession contract to revive the power plant, potentially converting it to a natural gas-fuelled plant to be supplied with gas from the planned Trans Adriatic Pipeline [10].

I believe that construction of an enlarged version of the existing combined cycle gas turbine (CCGT) up to 300 MW will help to strengthening Albania's energy infrastructure, reinforcing its risky supply from HPP and also can provide flexibility of the system. The remaining 1% (10 MW) of installed capacity in 2018 comprised small-scale (i.e., each less than 2 MW) solar photovoltaic (PV) plants. The import of electricity varies on weather conditions and historically 3TWh/year of electricity demand is imported from regional market [17]

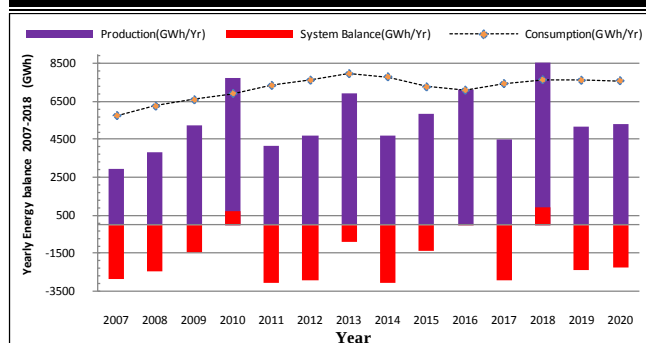


Figure 1: Yearly electricity balance in Albania (GWh), 2007-2020. [17]

The net domestic production of electricity realized for 2020 is 5,313 GWh. As can be seen in the graph in figure 1, the lowest electricity consumption recorded in our country is in 2007 with 5,767 GWh and the highest electricity consumption is the one recorded in 2013 with 7855 GWh. For 2020, electricity consumption in our country is 7,588 GWh. Compared to 2019, there is a slight decrease in electricity consumption in the country by 23.4 GWh. Generation of electricity for 2020 is about 9.7% lower than

average production for the 2009-2020 period. Despite the increase in production capacity during 2020 due to a bad hydrological year, the electricity production for this year has resulted in the amount of 5,313 GWh or 569 GWh less than average electricity production in the 2009-2020 period. This indicator clearly represents the high degree of hydrological risk in the production stability of electricity in our country, which bases the production of electricity mainly on hydro sources. [17].

Technical and non-technical losses still remain critical issues for the national power system accounting for around 21.7% of the total electricity consumption in 2019 [18]. Between 2014 and 2018, the amount of net energy imported varies from 12% of the TPES in 2015 up to 46% in 2017. Albania is the largest producer and exporter of oil in the South-East Europe region, most oil extracted in Albania is exported as unrefined crude oil [10]. A further contributor to net energy imports is the country's rising demand for petroleum products, largely fuelling the transport sector. Greening the transport sector by taking up biofuels blending and introducing electric mobility could lower the country's energy imports and positively contribute to the national economy.

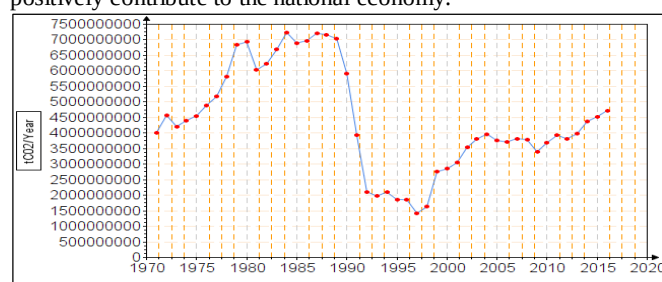


Fig. 2: Yearly variation of CO₂ in Albania [10].

In 2019, CO₂ emissions per capita for Albania was 1.93 tons of CO₂ per capita. Albania CO₂ emissions per capita fluctuated substantially in recent years, showing an increasing trend from 1970 up to 2019 period. By the end of 2019 the specific emission reached a value of 1.93 tons of CO₂ per capita.

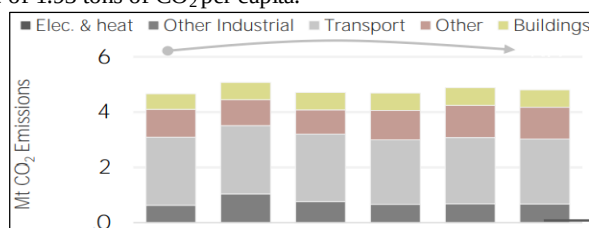


Fig. 3: Energy related CO₂ emission by sector in Albania [10].

Renewable energy sources, including solar, wind, hydro, biofuels and other future renewable sources are at the centre of the energy

transition towards a less carbon-intensive and more sustainable energy system [19]. In the context of GHG emissions, Albanian's electricity sector is zero emitter in the region as the share of electricity from renewable sources in total electricity generation is almost 100%, while EU-27 countries together have a RES share of 32.3% and the border countries Greece (30.3%), North Macedonia (35.1%), Montenegro (59.2%) and Kosovo highly depended on lignite has only 5.1%. The transport sector's energy demands are mostly met by oil and to a lesser extent by biofuels (87.9ktoe, 13.4% in 2017) [20]. However, no system is in place to guarantee the sustainability of the used biofuels [16]. Referring 2019, CO₂ emissions from fuel combustion accounted for the largest share of GHG emissions in Albania which apparently is dominated from road transport sector as the rail and others forms of transport are negligible (refer table 5). More than 75% of CO₂ emissions derived from diesel and petrol engines 41.6% and 34.2%, respectively [21]. The above information are very important and will serve as primary inputting data in EnergyPLAN model. The validation procedure follows recommendations given [1] and of the main outputs of the model are compared to that published by the national authorities in the country [14,17].

4.1 TRANSPORT SECTOR OVERVIEW IN ALBANIA

The Environmental pollution caused by the transport sector is one of the main problems, ranking Albania last in the Balkan region [7;22]. The total vehicle number in Albania referring to the national's statistic data [23] is 527,602 with a slight increase of 6.54% referring to 2015. The M1 vehicle category prevails making 77% of the total vehicle fleet in our country. The number of vehicles is increasing from year to year. Starting from 1998 the number of vehicles has changed from 42 vehicles/1,000 inhabitants to 124 vehicles/1,000 inhabitants as it is shown in Table 3.

Table 3: Specific vehicle number per 1000 inhabitants in the Balkan region [7]

	Nr. vehicle/1,000 inhabitants
Serbia	238
North Macedonia	155
BiH	214
Albania	124
Montenegro	309
Kosovo	na

In 2017, Tirana counted 233 vehicles per 1000 inhabitants but in national level the number of vehicles per 1000 inhabitant is increased to 147.

Table 4: Specific indicators by type of transport in Albania, 2014-2020[23]

Descrip tion	2015	2016	2017	2018	2019	2020
Total of freight and passenger vehicles	522,06	563,106	535,570	578,635	627,355	676,811
Road passenger vehicles	443,227	479,217	460,299	500,891	544,279	588,810

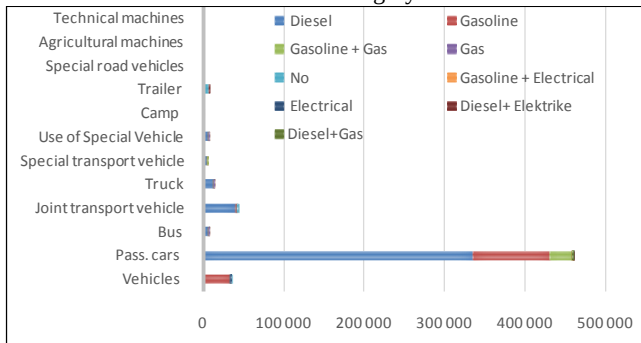
From table 4 it is observed that total of freight and passenger vehicles is 588,810. The passenger group constitute around 87% of the total.

The distribution of fuel consumption per each form of transport including road, air, railway and inland navigation is given in the table 5.

Table 5: Specific energy consumption) by transport type in Albania (ktoe) [24]

Transport	Railways	Road transport	Air transport	Inland navigation
832 (ktoe)	2.10	786.76	6.69	36.54
9.6772 (TWh)	0.024423	9.150	0.0778	0.4249

The total transport energy consumption referring [24] is 832ktoe. Road transport sector has an annual energy demand of 786.76ktoe and shares 94.5% of the total energy demand from transport sector. From the graph in figure 4 the distribution of each vehicle category by fuel type is given. The passenger category constitutes approximately 80% of the total vehicle number in our country followed by the motorcycles with a share of 6% and the rest comprises buses, trucks etc. Based in the numbers above the intervention and improvements for a better and sustainable transport sector should be addressed in this category.

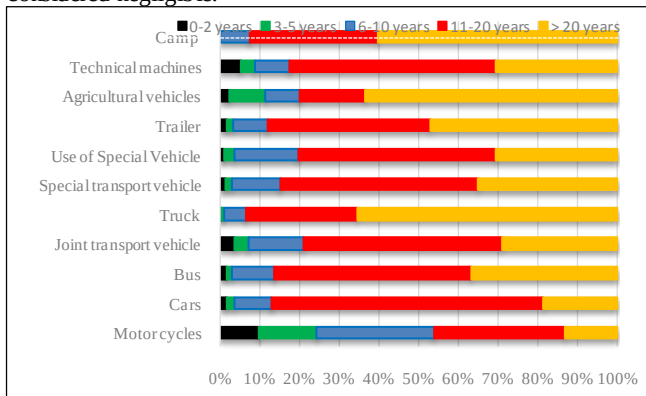
**Figure 4:** Distribution of vehicle category by fuel type, 2018.

From the graph in figure 4 the distribution of each vehicle's category by fuel type is represented. It is shown the wide range use of the diesel fuel powered engines. The heavy transport, buses and agriculture vehicles are totally diesel powered while vehicles category (motorcycles) are totally gasoline-based engines.

Table 6: Distribution vehicles by fuel used in transport sector in Albania [25]

Fuel type	%
Diesel	73
Gasoline	21
Gasoline-Gas	6
Diesel-Gas	Negligible
Gasoline-EV	Negligible
Diesel-EV	Negligible
Gas	Negligible
EV	Negligible

From the table 6 is depicted the distribution of fuel type within road transport sector. The diesel passenger vehicles constitute 0.73, petrol 0.21, and gasoline-gas constitutes 0.06 while other fuel powered engines have a small percentage, and its impact is considered negligible.

**Figure 5:** Vehicles by type and year of production, 2021 [25].

The number of vehicles age more than 20 years prevails in the category of trucks, joint transport vehicles, buses, camps and agriculture vehicles. The vehicle group of age of 11up to 20 years has the highest share within groups. The M1 category constitutes approximately 71% of the total vehicle fleet hence the main focus throughout the study is shown in this category, reflecting the same outputs of the study [7]. From technical point of view and public acceptance, the category M1 should be in the center focus of our analysis.

5 METHODOLOGY

Energy system models are used to provide challenges into possible 100% future energy supply options. For long-term models, it is common that time resolution is simplified, and energy production/consumption is often tracked by annual flows [26]. This works well for fossil fuels and most established energy technologies, which are typically characterized by high-capacity factors. However, the intermittent nature of many renewable energy sources and their electricity production characteristics require better time resolution to capture the dynamics in an electricity system with a significant share of RE [27;28].

5.1 MULTI-CRITERIA EVALUATION

Multi-criteria methods are widely used to assess sustainability in energy strategies and electricity mixes due to their ability to capture the complexity of socioeconomic and biophysical systems [29; 30]. Multi-criteria assessments are useful for complex issues with significant uncertainty, different perspectives, various data forms, and diverse stakeholder opinions [31]. A multi-criteria analysis is used to evaluate the sustainability and impacts of different electricity generation mix scenarios using five different criteria: (i) total costs (ii) total installed capacity (iii) excess electricity; (iv) CO₂ emissions; and (v) direct job creation. The first four criteria can be directly calculated from the EnergyPLAN model and the fifth can be calculated separately [26]. The employment factor method is not considered in this study but has been used in many earlier studies [32,33] to assess employment from power plants.

5.2 THE METHODOLOGICAL APPROACH FOR THE DEVELOPMENT OF SMART RENEWABLE ENERGY PENETRATION STRATEGIES ON TOTALLY FOSSIL BASED TRANSPORT SYSTEM.

Using the best scenario created after evaluation of the different electricity strategies, 3 new scenarios are created analysing the best national transport strategy with the main aim to convert from fossil-fuelled road transport system into a mixed powered one. Following this plan, the EV scenario presented in the methodology changes petrol and diesel fuel consumption in road transport for the corresponding electricity demand. To make this conversion, it is assumed that electric vehicles have an efficiency of 0.62 MJ/km (6km/kWh). For example, Tesla-Model X Standard Rang has a specific fuel 19.2 kWh/100km, while diesel and petrol vehicles have average efficiencies of 1.4 up to 1.5(MJ/km) and 1.8 up to 1.9(MJ/km), respectively. The transport distribution file is unknown and can be supposed constant throughout the year and added in the electricity cell demand for the reference energy system. The operating strategies of the reference system are modelled, simulated, and adjusted using EnergyPLAN modelling tool until the outputs correspond to that declared from official energy reports as it is given in the previous work [1]. Albania's biggest energy imports are fossil fuels fuelling the transport sector's energy demand, hence new alternatives and smart renewable energy strategies are proposed.

5.3 EnergyPLAN model

EnergyPLAN is an input/output deterministic energy system analysis tool (see Fig. 6 specifically designed to assist the design of national or regional energy planning strategies under the "Choice Awareness" theory [34]. The EnergyPLAN is a bottom-up model, a descriptive analytical model for medium/large-scale energy systems using multi-objective evolutionary algorithms to optimize solutions in the context of complex problems involving all consumption

demand and sectors. It can be employed to simulate and optimize energy systems with high shares of renewable energy on regional or national scales and has previously been used in a number of energy system analysis activities, including expert committee work for the Danish Energy Authorities and NGOs as well as the design of 100% renewable energy systems [35-37]. Both technical and economic optimization strategies can be provided from the EnergyPLAN modelling software.

The technical optimization aims to minimize fossil-fuel consumption without any cost considerations while economic optimization leading to the minimization of the total operational expenses. As indicated in [38] decision makers and researchers should choose the most suitable energy system modelling tool depending on the specific purpose and objectives of their analysis. A lot of studies by different authors in Ref. [39] and [40] have highlighted the possibilities of EnergyPLAN to construct long-term scenarios based on high-RES integration.

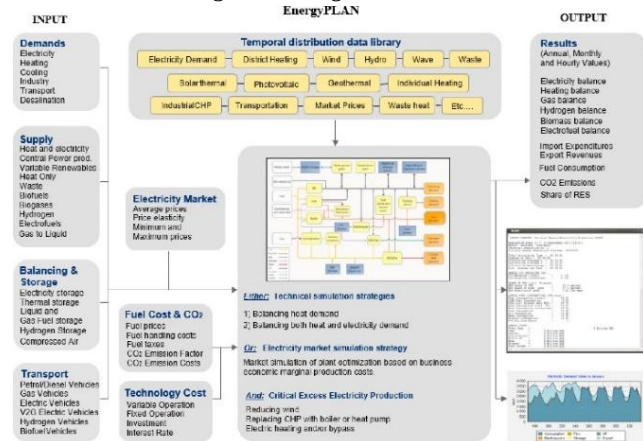


Figure 6: The overall technology and flow model on which EnergyPLAN is based (adopted from Ref. [34]).

Additionally, from this software it is possible to balance the energy system and to analyse how new smart strategies applied in one sector can affect others. The EnergyPLAN model has as general inputs, the demand, the renewable energy sources, the energy station capacities, the costs and the number of optional regulation strategies. Among the various outputs are energy balance and resulting annual production, fuel consumption, electricity import/export, total annual carbon dioxide emissions, RES share etc. Thus, with EnergyPLAN, the user can take a holistic approach focusing on the analysis of the cross-sectoral interaction. Traditionally disparate demand sectors, such as buildings, industry and transport, are linked with supply technologies through electricity, gas, district heating and cooling grids. In this way, EnergyPLAN enables the analysis of the conversion of renewable electricity into other energy carriers, such as heat, hydrogen, green gases, and electro-fuels, as well as the implementation of energy efficiency improvements and energy conservation.

This free model will help our work, as energy expert and planners to determine the annual reduction in the emission of greenhouse gases stemming from using the proposed technology in place of the base case technology. The model uses a computerized system with integrated mathematical algorithms and top to bottom approach which has been developed to overcome the barriers to clean energy technology implementation at the preliminary feasibility stage. The new model launched in 2021 by the developer offer an option to include other emissions than CO₂.

5.4 PROPOSED ROAD TRANSPORT SECTOR SCENARIOS

Transport demand is rapidly increasing leading to high dependence on fossil fuels, there would be serious consequences for human health and energy security-related issues as long as no measures are undertaken. Nonetheless, a couple of vital changes towards mobility are anticipated. [41].

These changes will be alternative fuel penetration, e.g., electricity, hydrogen, and renewable fuels such as synthetic fuels, but also biofuels to lessen conventional fuel usage. Technological efficiency and demand-side solutions are additional changes that are expected for the transport sector. Electricity can be used in direct form in all transport modes, though, with distinct emergence in each mode: in road and rail modes to a greater extent, and in marine and aviation to a lesser extent. Direct electricity-based transportation is one of the most promising technologies with high reliability, safety, and efficiency for mobility. EV's still have many limitations that have to be overcome to enable them to penetrate deeper into the market [42]. Hydrogen as fuel for the transport sector can be produced from electricity through water electrolysis processes or fossil fuels which at present it is mainly based on NG and converted via steam methane reforming (SMR) (non-sustainable fuel) and Hydrogen will exist in all transport segments due to its flexible usage via fuel cells. Biofuels such as bioethanol, bio-methanol, and biodiesel produced from biomass sources can directly substitute current fossil-fuel demand.

The road mode is one of the most attractive transport segments to be electrified. There are developed four different types of EV: Battery-electric vehicles (BEV), hybrid electric vehicles (HEV), and plug-in hybrid electric vehicles (PHEV) have shown high growth rates in recent times and FCEV typically using hydrogen to generate electricity that flows to the power module (electric motor) to turn the wheels [43]. The internal combustion engine (ICE) is the dominating power train as of today, but the limited efficiency of around 26 up to 30% reduces the competitiveness of this kind of engine era and the exit from the market comes due to the rising concerns about air pollution. HEV has almost the same complexity as ICE with an electric motor/generator and a battery to improve the efficiency of the system. This hybridization makes it feasible to benefit from regenerative braking to generate electricity and charge the battery, which improves the efficiency to some extent. In this research, there is no focus on HEV, though PHEV is regarded. PHEV has the same features as a HEV, but the battery is generally larger and can be charged from the power grid for a range of typically from 50 up to 80 km. Therefore, it would be possible to use PHEV daily mainly on an electricity basis for reducing the overall fuel cost, and hence improving fuel economy. PHEVs are not zero-emission vehicles, since fossil fuel is still used, but it has been observed that about 70% of all driven kilometres could be electric and only 30% are typically based on fossil fuels, which can drastically reduce GHG emissions, in particular if fossil-fuel-free electricity is used. BEVs are vehicles type that rely solely on electric propulsion and consist of comparable components to PHEV, though without the ICE and higher battery capacity, and it could use a more powerful electric engine. Most BEVs currently offered to the market have a range of 100 up to 250 km on a single charge with the highest range up to 550km. Charging time is a peculiar drawback for BEV, depending on charger configuration, its infrastructure, and operating power levels. Similar to BEVs, a fuel-cell electric vehicle (FCEV) uses an electric drive train, wherein the vehicle is powered by a fuel cell, typically using hydrogen to generate electricity that flows to the power module (electric motor) to turn the wheels.

The baseline model is based on the energy consumption without any intervention in the fuel type diversification by 2030. The baseline model will have an annual demand of 13.96TWh referring to [14] and is compared with 3 alternative scenarios. All the distinctive features are analysed in detail, and the demands of the different sectors are identified as well as the potential modifications and potentially exploitable energy supply sources in each of them.

Table 6: Proposed Road Transport Scenarios, Albanian case.

Scenario	
Baseline Scenario	-
Scenario 1	Biofuel
Scenario 2	EV
Scenario 3	Combined (Biofuel+EV+H2)

6 SIMULATION AND RESULTS

Albania's biggest energy imports are fossil fuels fueling the transport sector's energy demand. The transport sector's energy demands have been rising, and the sector is projected to continue to be the largest energy consumer over the coming decades. With this rising demand, given fluctuating oil prices and strong import dependence, a move towards greening the transport sector would provide a more economical and environmentally sound way to meet the sector's energy demands. This could be achieved by incentivizing the use of electric vehicles and enforcing mandatory biofuel blending. A prerequisite for biofuel blending is an established sustainability criteria that would ensure an environmentally sound use of biomass for energy. Furthermore, given that 41% of agricultural land in Albania lies fallow [44], inland potential for sustainable local production of biofuels is worth assessing. Developing this would benefit the local economy and reduce the need for imports. Additionally, electric mobility can support the electricity sector's development through load peak shaving or load shifting, which offsets peak loads to off-peak hours and alleviates overloading of the grid. This in turn can reduce distribution power losses, increase distribution power quality and extend the lifetime of the power infrastructure, while also reducing power generation costs.

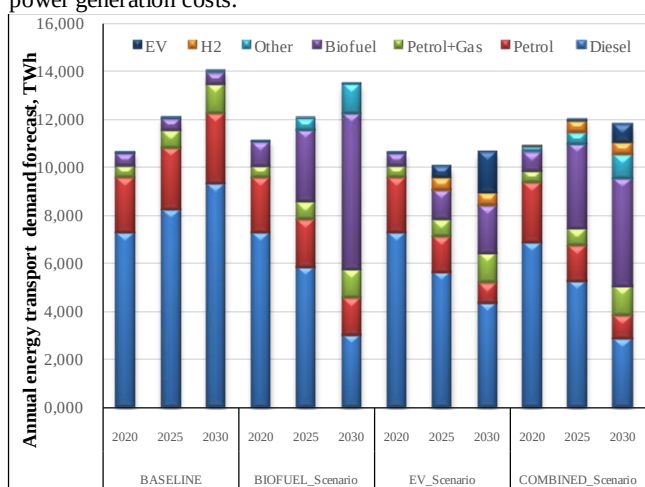


Figure 7: Annual energy consumption from road transport under different scenarios. (TWh).

From the graph in figure 7 the annual energy demand under different scenarios and fuel type is given. The total annual consumption varies, and the efficiency of each technology is considered.

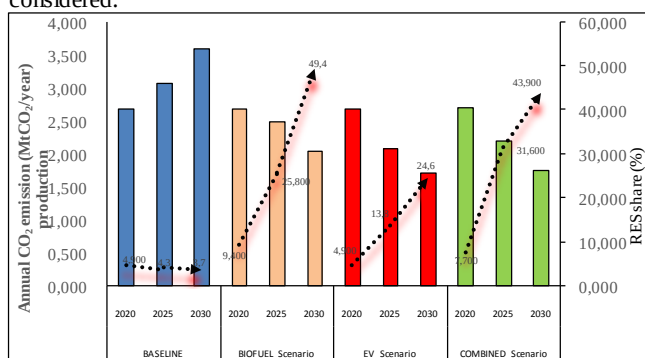


Figure 8: Annual predicted CO₂ emission (MtCO₂/year) and RES share within transport sector alone (%) under different scenarios.

In figure 8 the simulation results from EnergyPLAN are given per each of the three scenarios. Combined scenario results the most profitable as it has the highest RES share promoting EV, Biofuel and H₂ by the end of 2030.

The diversification of energy sources within transport sector is the main key to the decarbonisation process in Albania. The three scenarios included in this study have their environmental and social

impact and will be further studied in the extended version of the paper.

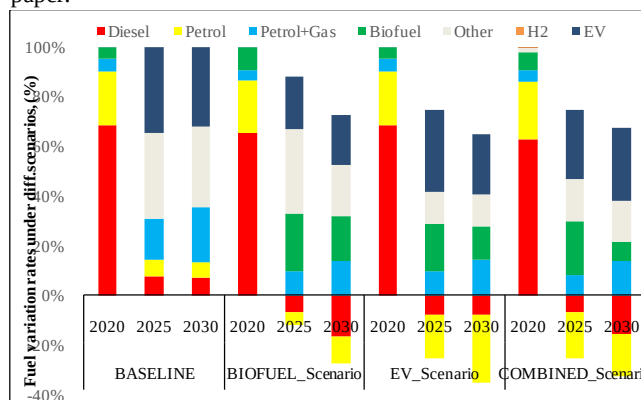


Figure 9: Fuel change ratio in % under different transport scenarios 2020-2030 in Albania.

The fuel change rate (%) referring to 2020 transport fuel distribution for different scenarios is given in the graph in figure 9. The decrease of fossil fuel is obligatory to meet a reduction rate of CO₂ by 11.5% in 2030.

The predicted annual consumption from EV varies from 0.001049TWh up to 1.7 TWh. In the combined scenario, EV will constitute 17% of the total transport energy consumption while in the EV scenario it will share 36.34%. In both cases the PV modules options and other factors that influence the electricity distribution demand, the numbers of vehicles travelling to the fuel stations, battery capacity and energy required to charge one car each day in a year bases to calculate the PV modules and parking area is required.

7 CONCLUSION

Albania face conflicting demands for transport policies as the demand is increasing continuously. Promoting healthy and sustainable transport options prevents the negative effects of current transport patterns on human health. Cooperation among sectors and high-level political commitment, incentives schemes to promote a sustainable transport sector are crucial and should be at the center of energy transition process in Albania.

A prerequisite for biofuel blending is an established sustainability criteria that would ensure an environmentally sound use of biomass to meet transport energy demand. Furthermore, given that a lot of agricultural land in Albania lies fallow, so that incentives to promote inland potential for sustainable local production of biofuels is worth assessing.

As a conclusion, the most profitable scenario results combined one as biofuel is a promising renewable energy source and the country has available huge potential of biomass to cover the transport demand in 2030. This scenario will provide 43.9% RES share by 2030 (referring energy consumption within transport sector) integrating promising future transport technologies based such as: H₂, EV and biofuel leading to a diversified transport sector based on renewables.

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Impact of tourism income generated from the introduction of innovation on macroeconomic indicators in Turkey

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Abstract: This article presents a calculation model based on the impact of tourism services and income of hotel enterprises, which have a special share in this service, on the gross product, GDP, labor resources, capital investment and working capital through econometric models. It assesses labor resources, GDP, investment in fixed capital and key indicators for the development of the tourism complex of the Republic of Turkey and provides relevant forecasts. In addition, the statistical significance of the model based on the Eviews software package was checked and its suitability for forecasting purposes was determined.

KEYWORDS: MACROECONOMIC INDICATOR, SOFTWARE PACKAGE, TOURISM SECTOR, MODEL, ADEQUACY, INCOME, CORRELATION, RECESSION, CAPITAL.

1. Introduction

Modeling the country's macroeconomic indicators based on macroeconomic processes and forecasting for future periods is one of the effective tools for analyzing the factors affecting the formation of a country's GDP and determining the ways of its development. One of the main ways to study the effectiveness of tourism services in the field of economic activity is an approach based on the application of econometric models of macroeconomic indicators. Econometric models create more favorable conditions for the analysis of cause-and-effect relationships between variables, mainly for large-scale research, their forecasting, construction of economic policy scenarios (options) based on simulation experiments with models and selection of optimal options. Obviously, accurate forecasting of macroeconomic indicators with the help of econometric models, taking into account limited resources, is an effective tool for analyzing the country's economic development potential.

2. Main indicators of the tourism system of the Republic of Turkey

Need for forecasting at the level of economic systems is these systems are constantly changing under the influence of the external environment (natural phenomena, market conditions, economic crises, inflation, etc.). Introduction of innovation in this sector plays a large role in the development of the tourism sector in Turkey. Therefore, when developing management strategies in connection with the current state of the external environment, it is always necessary to effectively use a database that is adequate to these conditions. In essence, forecasting allows to assess the expected state of environmental factors to which the economic system is exposed, playing the role of reducing the risks associated with uncertainty.

In the study, the gross domestic product is determined using the Cobb-Douglas production function as follows.

$$GNP(t) = a * L^{\alpha}(t) * K^{\beta}(t) * M^{\chi}(t) \quad (1)$$

Here, GNP is an indicator of GDP in t years;

L - labor force indicator;

K - indicator of capital investment in fixed capital or fixed assets;

M - indicator of current assets;

a, α , β , χ – are the parameters of production functions evaluated by the method of least squares.

Functions of production consist mainly of mathematical elements that reflect the dependence of the results of production on the consumption of resources, and determine the mechanism of behavior of the economic system as an argument and a function. [1] At the micro level, the input elements of the economic system are K-production funds (capital reserves) and L-labor resources. In this case, in general, the nonlinear production function $y = F(K, L)$ can be considered a model of the economy. This means that production can be interpreted as a function of consumption of resources.

Cobb-Douglas production function, which is a special case of a multiplicative production function, is defined by a general formula

$$Y = AK^{\alpha_1}L^{\alpha_2} \text{ or } Y = AK^{\alpha}L^{1-\alpha}$$

Here, A is the neutral coefficient of technical progress,

α_1 - the coefficient of elasticity of funds ($\alpha_1 = \alpha$),

α_2 - the coefficient of elasticity of labor ($\alpha_2 = 1 - \alpha$). [2]

That is, the coefficient α_1 is the elasticity of production in the economic system for fixed assets, and the coefficient α_2 - for living labor.

Coefficient α_1 characterizes the percentage increase in production with 1% increase in fixed assets, and coefficient α_2 characterizes the percentage increase in production volume with 1% increase in live labor costs. [2] Obviously, if $\alpha_1 > \alpha_2$, then intensive development will prevail in the economic system, and vice versa, extensive development will prevail.

3. Gross domestic product (GDP) is important of the macroeconomic indicators.

It should be noted that in most developed countries, GDP, which reflects the total market value of all goods and services produced in the country, differs from the gross national product (GNP), which reflects the total market value of all goods and services produced by the citizens of the country using their own factors of production not more than 1% [3]. Global gross domestic product is about \$75 trillion, of which Turkey's GDP is only 1.13%. In the United States, the figure is 18%, and in China it is 17.6%. Also, according to forecasts, China can replace the United States in 2030 with the highest GDP level.

Although Turkey's trade turnover increased by \$37.3 billion in 2017 compared to 2016, GDP decreased by 1.3% or \$ 11.73 billion. The table below shows Turkey's key macroeconomic indicators for 2016-2017.

Table1. Turkey's main macroeconomic indicators

Main macroeconomic indicators	2016	2017
GDP (\$ billion)	862,774	851,046
GDP growth (%)	2,6	7,4
GDP per capita (\$)	10 807	10 597
Industrial production index	126,6	130,0
including in the processing industry	127,5	131,4
Agricultural production index	9,3	9,9
Fixed assets investments (million Turkish lira)	190,260	514,222
Consumer price index (in %)	8,53	11,92
Economic and unemployment	10,9	10,8

rate, %		
Employment rate (%)	0,3	0,3
Budget deficit / GDP surplus, %	-1,14	-1,52
International reserves, \$ billion	106,108	107,619
Other reserves, \$ billion	0	0
Dollar exchange rate of the national currency	3,02	3,77
Euro exchange rate of the national currency	3,69	3,99
Share of public debt in GDP, %	29,1	28,2
National Bank discount rate, %	7,25	7,25
Retail trade turnover, (\$ billion)	72,3	73,5
Retail sales index	129,5	131,1
Trade turnover, \$ billion	341,2	378,5
Exports of goods, \$ billion	142,6	156,5
Imports of goods, \$ billion	198,6	222,0
Total export of services (\$ million)	37 235	43 925
Balance of other trade services (\$ million)	-1 706	-1 623
Foreign direct investment in Turkey, \$ billion	12,1	5,0
Domestic investment in Turkey, \$ billion	6,1	7,4
Credit rating (according to Standard & Poors) BB + BB +	BB+	BB+

Source. Compiled by the author according to the Turkish State Statistics Institute.

As can be seen from the data in the table, due to decrease in GDP, GDP per capita also decreased by \$210. The decline in GDP is due to the depreciation of the national currency against the dollar and the euro. Unemployment rate of the economically active population decreased by 0.1% to 10.8% compared to the previous year. Turkey's international reserves also increased by \$1.511 billion to \$107.619 billion. Despite a decrease of \$7.1 billion in foreign direct investment in Turkey compared to 2016, the volume of domestic investment increased by 21.3% compared to the previous year. The low discount rate of the National Bank compared to some neighboring countries (7.2%) resulted in the country's credit rating being BB +. Total service exports in 2017 increased by \$6690 billion compared to 2016 and amounted to \$43925 billion. Share of tourism in total service exports was 51.2%, and in total service imports was 20.3%. These indicators are reflected in the table below for 2013-2017.

Table2. Trade services in the Republic of Turkey for 2013-2017, (\$million)

Years	2013	2014	2015	2016	2017
Total service exports	46 638	50 506	46 225	37 391	43 925
Transport	13098	14361	14142	13110	15462
Tourism	27997	29552	26616	18743	22478
Construction services	675	1084	374	512	474
Insurance services	1000	1154	1124	1159	1251
Financial services	779	824	658	676	631
Other trade services	602	535	250	622	883
Public services	798	826	826	616	610
Other services	1689	2170	2083	1746	1768

Total service imports	21 158	22 581	22 266	22 128	23 792
Transport	9821	10121	8227	8077	9832
Tourism	4817	5072	5368	4783	4823
Construction services	0	0	0	0	34
Insurance services	1718	1651	1566	1676	2014
Financial services	1334	1903	1779	1610	1192
Other trade services	2554	2353	1765	2340	2506
Public services	1686	2324	1902	1788	1394
Other services	1558	1354	1259	1328	1372

Source. Calculated according to the Central Bank of Turkey

As can be seen from the table of trade services in the Republic of Turkey for 2013-2017, share of tourism in total service exports in 2014 increased by 5.5% compared to the previous year and amounted to 58.5%, but decreased in subsequent years. On the contrary, the share of tourism in total service imports developed with increasing dynamics in 2013-2017.

4. Impact of income from Turkish tourism services on GDP in Turkey.

Table3. Revenues from tourism and GDP dynamics in the Republic of Turkey

Years	Revenues from tourism, \$ bln (X)	GDP, \$ bln (Y)
2001	13,45	200,31
2002	15,21	238,34
2003	16,3	311,94
2004	20,26	404,85
2005	24,12	501,16
2006	23,15	550,8
2007	27,21	675,01
2008	30,98	764,64
2009	32,01	644,47
2010	33,03	772,29
2011	36,15	832,5
2012	36,46	873,7
2013	39,23	950,33
2014	41,41	934,08
2015	41,62	859,45
2016	31,36	863,39
2017	38,62	851,52

Source. Compiled by the author according to the Turkish State Statistics Institute.

To analyze the regression of the relationship between income from tourism and GDP for 2001-2017, data from table 2 and ready-made packages of mathematical programs EViews, MatLab, MS Excel, MathCad and others are used. For this purpose, using the software package Eviews, we obtain following result based on data in Table 2.

Table4. Results of the regression analysis of the relationship between tourism income and GDP in the Republic of Turkey according to the Eviews application software package

Dependent Variable: Y

Method: Least Squares

Date: 01/20/19 Time: 18:29

Sample: 2001 2017

Included observations: 17

Variable	Coefficient	Std. Error	t-Statistic	Prob.
X	25.83377	1.805334	14.30969	0.0000
C	-100.0706	55.58623	-1.800277	0.0920
R-squared	0.931746	Mean dependent var	660.5059	
Adjusted R-squared	0.927196	S.D. dependent var	248.6519	
S.E. of regression	67.09193	Akaike info criterion	11.36014	
Sum squared resid	67519.91	Schwarz criterion	11.45816	
Log likelihood	-94.56115	Hannan-Quinn criter.	11.36988	
F-statistic	204.7672	Durbin-Watson stat	2.430765	
Prob(F-statistic)	0.000000			

Source. developed by the author based on the Eviews software application

Based on the results obtained in the Eviews application software package, regression equation will be as follows:

$$Y = 25,83377 * X - 100.0706 \quad (1)$$

According to the data in Table 2, if we build a correlation matrix in MS Excel application software package, we get the following table:

Table 5. Correlation matrix

	Y	X
Y	1	0,96527
X	0,96527	1

Source. developed by the author based on the MS Excel application

As can be seen from the table 5, there is a very high direct relationship between the Y and X variables on the Chedok scale (0.7-0.9) ($R_{yx} = 0,96527$).

Determination coefficient obtained based on the Eviews application software package ($\sqrt{R^2} = 0,96527 = 0,98248$).

Dynamics of the Fitted and Actual values obtained by the Eviews application software package with the regression equation of the model (1), as well as the residuals between them, are given in the graph below.

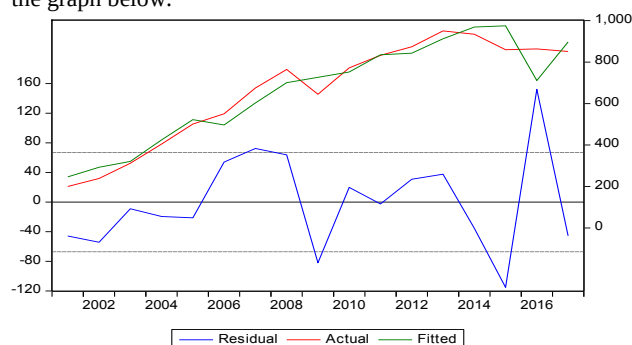
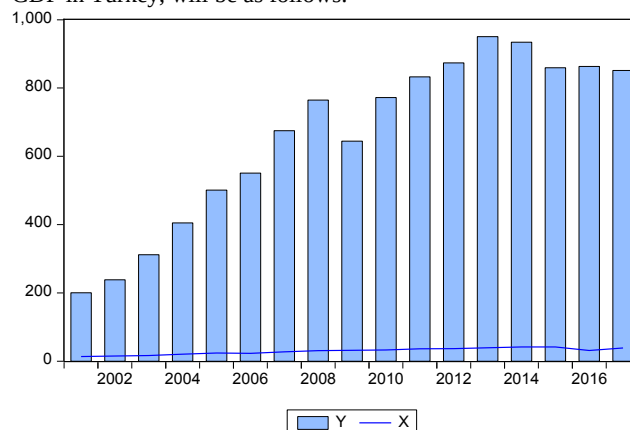


Fig1. Dynamics of the Fitted and Actual values

According to the graphical Eviews application software package, which reflects the dynamics of income from tourism services with GDP in Turkey, will be as follows.



Source. developed by the author based on the Eviews application

For linear regression obtained by double correlation $y = \alpha_0 + \alpha_1 x = 25.83377 * X - 100.0706$, we calculate the elasticity coefficient, which expresses the percentage change in the dependent variable as a result of a change in 1% of the free variable. This ratio is calculated according to the following formula.

$$E = \frac{\alpha_1 \bar{x}}{\bar{y}} \quad (2)$$

Here, α_1 is the coefficient of the contact equation shown above.

($\alpha_1 = 25,83377$)

$\bar{x}$ - calculated average of GDP in Turkey for the studied periods, ($\bar{x} = \frac{\sum x}{n} = 29,44529$)

$\bar{y}$ is the calculated average of income from tourism services for the studied periods ($\bar{y} = 646,4965$)

Based on these indicators, the coefficient of elasticity will be as follows.

$$E = \frac{\alpha_1 \bar{x}}{\bar{y}} = \frac{25,83377 \times 29,44529}{646,4965} = 1,176624$$

As a result of the report, it can be concluded that 1% increase in revenues from tourism services for the period under review resulted in 1.18% increase in GDP in Turkey.

5. Conclusions

Thus, based on the econometric assessment of the impact of tourism revenues on GDP in Turkey, it was determined that 1% increase in tourism revenues for the period under review resulted in 1.18% increase in GDP in Turkey. According to the results obtained in the Eviews application software package, there is a very high correlation between income from tourism services and GDP, which is close to the functional dependence expressed by the regression equation. According to the results obtained in the Eviews application software package, about 96.3% of GDP in Turkey for 2001-2017 is due to changes in revenues from tourism services. GDP growth was 3.7% under the influence of other factors. The amount of GDP and standard errors found by the regression equation obtained according to the Eviews application software package, as well as the characteristics of the use of the equation for forecasting purposes are determined by a graph. Based on these characteristics, income from tourism services in the Republic of Turkey can be forecasted for any period, depending on GDP.

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Advances in reducing formaldehyde emission from wood-based panels

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Abstract Formaldehyde emission is one of important issues in the wood-based panel industry. Recently, many countries tighten regulations on formaldehyde emissions emitted from wood-based panels due to harmful effect of formaldehyde on the humans. Urea-formaldehyde (UF) resin is the most used synthetic resin as binder in the production of wood-based panels for indoor applications. Disadvantages of UF resin are the formaldehyde emission and low water resistance. UF resin is classified according to the formaldehyde releases, Super E0, E0, E1, and E2, which are from lowest to highest, respectively. Many researchers have focused on the synthetic and natural formaldehyde scavengers for decreasing the formaldehyde emission from the wood-based panels. In this study, recent studies for reducing formaldehyde emission from wood-based boards were reviewed.

KEYWORDS: FORMALDEHYDE EMISSION, WOOD-BASED PANEL, UREA-FORMALDEHYDE, SCAVENGERS

1. Introduction

Formaldehyde is considered a health hazard, hence wood-based panels must be within the limits imposed by the strictest regulations in terms of formaldehyde release. Formaldehyde is the first member in the homologous series of aldehyde. It is the colorless gas with sharp scent that irritates the mucous membrane of the nose and throat. Wood industry has already reduced formaldehyde emission of raw panels (uncoated) by more than 80% over the past twenty years to minimize indoor air contaminants [1]. Urea-formaldehyde (UF) is the most used synthetic resin in the production of wood-based panels used indoor applications due to its significant advantages such as low-cost, easy supply, transparent color, lower hot pressing temperature, and duration, good mechanical properties of the board in dry conditions. Despite of the mentioned significant advantages, UF resin has two main drawbacks, formaldehyde emission from the wood-based panel, and low water resistance in humid environment. UF resin is mainly responsible for the formaldehyde emission from wood-based panels [2]. For indoor and furniture applications, a lower formaldehyde content is required, if classified under the E1 emission class.

According to International Composite Board Emission Standards (ICBES), there are 3 European formaldehyde classes, namely, E0, E1 and E2. This classification is based on the measurement of formaldehyde emission levels. For instance, E0 is classified as having less than 3 milligrams of formaldehyde emission of every 100 grams of wood based panel. E1 and E2, conversely, are classified as having 9 and 30 grams of formaldehyde per 100 grams of the panel, respectively. All around the world variable certification and labeling schemes are there for such products that can be explicit to formaldehyde release, like that of Californian Air Resources Board (CARB).

Table 1. CARB phase 2 formaldehyde limits [3].

Product	Allowable Formaldehyde Concentrations
Hardwood plywood	0.05 ppm
Medium density fiberboard	0.11 ppm
Thin medium density fiberboard	0.13 ppm
Particleboard	0.09 ppm

Parameters affecting formaldehyde emission from particleboard produced using UF resin [4] :

1. Tree species and wood acidity
2. F/U molar ratio of UF resin
3. The amount of resin used

4. Density and thickness of particleboard
5. Hardener type and content
6. Free-formaldehyde content in the UF resin
7. Moisture content of mattress
8. Moisture content of finished panel
9. Hot pressing parameters (temperature, time, and pressure)
10. Environmental conditions (humidity and temperature) for finished particleboard
11. Overlaying of particleboard

The proposed formaldehyde emission reduction solution is summarized below [5].

- To change the molar ratio of U/F in glue production,
- Chemical formaldehyde bonding materials (urea, tannic acid, amine, ammonia, melamine and cyanoguanidine)
- Development of new glue formulations,
- The usage of alternative adhesives (phenol formaldehyde, isocyanate) to urea formaldehyde adhesives,
- The usage of plant and animal-based glues,
- Nanotechnology and plasma applications,
- Changing production conditions (such as press temperature and pressure)

The materials releasing formaldehyde in a room are shown in Figure 1. Especially, furniture is one of the most important materials on the formaldehyde release because it is produced using UF resin.

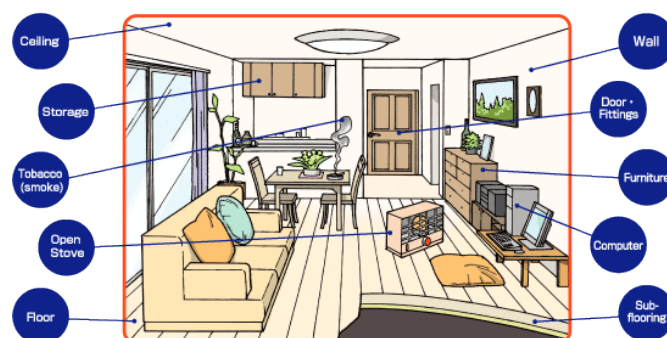


Fig. 1. Materials releasing formaldehyde in a room [6].

The formaldehyde emission standards for different countries are given in Table 2

Table 2. Current formaldehyde emission standards for wood-based panels in Europe, Australia, the USA, and Japan [32].

Country	Standard	Test method	Board class	Limit value
Europe	EN 13986	EN 717-1	E1-PB,	≤ 0.1 ppm
		EN 120	MDF, OSB	≤ 8 mg/100 g o.d. board
		EN 717-1	E1-PLW	≤ 0.1 ppm
		EN 717-2		≤ 3.5 mg/(h.m ²)
		EN 717-1	E2-PB,	> 0.1 ppm
		EN 120	MDF, OSB	$> 8 \leq 30$ mg/100 g o. board
Australia & New Zealand	AS/NZS 1859-1 & 2	AS/NZS 4266.16 (Desiccator)	E1-PB	≤ 1.5 mg/L
				≤ 1.0 mg/L
			E2-PB, MDF	≤ 4.5 mg/L
				≤ 0.5 mg/L
USA	ANSI A 208.1 & 2	ASTM E1333 (large chamber)	PB	≤ 0.18 or 0.09 ppm
			MDF	≤ 0.21 or 0.11 ppm
Japan	JIS A 5908 & 5905	JIS A 1460 (Desiccator)	F**	≤ 1.5 mg/L
			F***F*E0*	≤ 0.5 mg/L
			F****F*SE0*	≤ 0.3 mg/L

PB: particleboard; MDF: medium density fiberboard; OSB: oriented strand board
 F** class in Japan more or less equivalent to European E1-class
 F*** and F**** are of much lower emission than the E1
 F**** emission is close to the emission of solid untreated wood

There is a direct relationship between the formaldehyde emission and the formaldehyde content of the resin. The resin producers have focused on the reduction in the F/U molar ratio in the last decades to decrease formaldehyde emission from wood-based panels. Nevertheless, the reduction in the formaldehyde content in the UF resin decreases the reactivity of UF resin, which adversely affects the mechanical properties and dimensional stability of the panels. Another strategy is the use of scavengers. Natural or bio-based substances such as pozzolan, tannins, charcoal, starch, chitosan, and chemical compounds such as primary and secondary amines, sodium sulfites, borax, and ammonium phosphates have been tested [7].

2. Applications for decreasing the formaldehyde emission from wood-based panels

Hot press parameters, press temperature, time, and pressure, affects the formaldehyde and VOC emissions from the wood-based panels and they decrease with increasing severity of the pressing parameters. Furthermore, the panel manufacturers use powder urea as formaldehyde scavenger, which is added into the UF resin solution. It is one of the most commonly used formaldehyde scavenger is urea, mainly as aqueous solution, due to its low cost and good performance [8]. Wood based panels with low-formaldehyde emission can be produced using methyl-diphenoldiisocyanate (PMDI) adhesive.

In literature, of some natural scavengers such as paper sludge [9], chestnut shell flour [10], condensates obtained from kiln-drying of wood [11], phenolated kraft lignins [12], tannins extractives [13], soy flour [14], Chitosan [15], pine cone flour [16]. Zhang et al. [17] reported that formaldehyde emission of coated medium density fiberboard panels could be reduced by cold air and ammonia plasma treatment by 21% and 31%, respectively. Cold plasma treatment as an efficient and environmentally friendly method, which was completely different from the conventional formaldehyde scavengers, can significantly reduce the formaldehyde emission without decreasing bond performance of wood particles or fibers. In addition, the charcoal has a considerable impact on the amount of formaldehyde released by the manufactured boards. Kowaluk et al. [18] reported that the 50 wt% content of charcoal caused about 80% reduction of formaldehyde emission. Ayrlmis et al. investigated the potential utilization of such condensates from oak, beech and walnut, which were obtained in a 7.8 MHz vacuum dryer. The condensate was replaced with the deionized water (5%) in the production of urea-formaldehyde (UF) and melamine-urea-formaldehyde (MUF) resins in the reactor. The formaldehyde emission from particleboard and medium density fibreboard decreased significantly with addition of the condensate into the UF and MUF resins. Previous studies reported that some synthetic scavengers such as propylamine

[19], ammonium pentaborate [20] and ammonium bicarbonate [21], aluminium oxide [22], melamine, polyvinyl alcohol, and adipic acid dihydrazide [23] were effective to decreased the formaldehyde emission from the wood-based panels. Furthermore, Réh et al. [24] reported that beech bark flour decreased the formaldehyde emission from plywood by up to 74% without decreasing the mechanical properties of the wood-based panels. Bark of some wood species such as walnut and chestnut contains the high amount of phenolics, which may decrease the formaldehyde emission from the wood-based panels when the bark flour was added into the UF resin mixture [25,26].

Effect of nanofillers (titanium dioxide) as scavenger on the formaldehyde emission of E0 grade UF using at 0.5%, 1%, and 3 wt% based on the oven dry weight of UF resin was investigated by Park and Lee [27]. Costa et al. [28] investigated the effects of sodium metabisulfite, ammonium bisulfite, and urea on the technological properties and formaldehyde emission of particleboard. Among the scavengers, the sodium metabisulfite was the best additive giving the particleboards with zero formaldehyde emission. Dudkin et al. [29] added aluminum oxide nanoparticles in the UF resin to decrease the free-formaldehyde. Chotikhun et al. [18] determined the formaldehyde emission and mechanical properties of the particleboards produced from Eastern redcedar using silicone dioxide (SiO₂) nanoparticles added modified starch as a binder [31]. Nine different particleboards were produced with nanoparticle contents of 0%, 1%, and 3% at three density levels of 600, 700, and 800 kg/m³. The results showed that the nanoparticle content above 1% adversely affected the mechanical properties of the particleboard. Very low formaldehyde emission value of 0.07 ppm was determined for the particleboards.

Effect of nanocellulose on the formaldehyde emission wood-based panels was also investigated by Ayrlmis et al. Three grades of liquid urea-formaldehyde (UF) resins such as super E0 (SE0), E0 and E1 were modified by adding different amounts of microfibrillated cellulose (MFC, 5 wt%). The incorporation of the MFC into the SE0 up to 30 wt% significantly decreased the formaldehyde emission from of the UF resin while this riot observed for E1 and E1 grade resins. The total volatile organic compounds (TVOCs) of the LVLs considerably decreased with increasing MFC content at 25 °C and 35 °C.

3. Conclusions

Formaldehyde emission is one of the important characteristics of wood-based panels which limits their use in indoor application. There are different ways to reduce the formaldehyde emission from the wood-based panels. The most widely used two methods are to decrease formaldehyde/urea ratio and add the formaldehyde scavengers. Recently, use of environmentally friendly and sustainable formaldehyde scavengers in the production of wood-based panels has increased. Although only E1 grade wood-based panels are accepted by the many countries, it is expected that the use of E0 panels will increase in near future in the market.

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Renovation of worn surfaces of equipment in the metallurgical industry

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Abstract: The paper presents the possibilities of renovation of worn functional surfaces of roll for continuous steel casting. The cylinder was made of steel 24CrMoV55 - DIN 17240. The lifetime of the continuous casting line roll is limited by the quality of their functional surface. The worn roll is decommissioned and the extent of its damage has been assessed. Cracks are a limiting factor in deciding on its renovation. Renovation of functional surfaces of roller from a diameter of $\varnothing$ 200 mm is realized by technology submerged arc welding (SAW). The article presents the results of research into the quality of newly formed cladding layers. Their quality was evaluated using non-destructive and destructive tests. Based on the performed experiments, it can be stated that the used surface renovation procedure is suitable for the renovation of functional surfaces of continuous steel casting rolls.

Keywords: RENOVATION, SURFACE, WEAR, STEEL PRODUCTION

1. Introduction

At present 92,8% of the world's steel production is cast by the continuous casting machine. [1] For the steel production the rolls of the continuous casting play the primary role. Their role is to carry out the deformation of the casting steel and to guide the cooling steel strip from crystallizer in the route of the fluent casting. The rolls of the continuous casting lines are exposed to the combined wearing out. The abrasive wearing out is dominant which has the secondarily influence on the adhesive wearing out using the cycling exposing under the high temperatures in the corrosive conditions (Fig.1). These tribodegradation factors have a significant influence on the operating life of the rolls of the continuous steel casting installed in tracks of the fluent casting. [2,9,10] Several hundreds of the rolls are installed in the lines of the continuous steel casting there. Caster roll life can become the limiting factor for efficient long run slab caster operation. [3] With such a number of the rolls a 100% reliability is a must. The amount of the rolls itself presents the high part of the expenses for the operation, that's because the rolls are renovated if it is possible. Not all of the rolls could be renovated. Choosing the rolls for the renovation has to undergo the strict control which approves or disproves the convenience of the roll. The renovations are mostly done with completing the absent material, where the material with better quality, compared to the original material, can be used. [4, 8] Then the operation life of the renovated component can be longer than the original one. It has been possible to renovate the rolls three times so far. Then the rolls are subsequently excluded from the operation. The criterion for the wearing out of the rolls is the wearing out of the surface more than 1 mm on the roll average or a development of the corrosive-fatigue cracks more than 4 mm deep where is a danger of later breaking of the roll and the interruption of the casting machine operation. The rolls of the continuous casting work in the really aggressive conditions. These conditions are caused by the reaction of the free hydrogen ions with slag from the casting powder with the high content of the fluor. On the roll surface the corrosive pittings are made as the central points for creating the fatigue cracks. If there is the high content of the chlorine ions in the cooling water, they become „the driving force“ for their spreading in the crack's root. Because of these reasons the rolls are actually exposed to the corrosive weariness, adhesive-abrasive wearing out. [7]

The roll renovations use two most famous methods. For the rolls with the diameter up to $\varnothing$ 200 mm the technology of the flux-cored arc welding (FCAW) surfacing is used as it is the most convenient for such diameters. For the rolls with the diameter over $\varnothing$ 200 mm the SAW method (Submerged arc welding) is more convenient. Each of these technologies has its own advantages for the given diameters.

The rolls used in the lines of the continuous casting are renovated after the wearing out. It has been possible to renovate the roll three times so far. Afterwards the roll has been excluded. To save the materials, there has been the effort to apply the four cycles of surfacing whose results are presented in the article.



Fig. 1: The surface of the worn-out roll $\varnothing$ 300 mm

2. Experimental materials and methods

The analysis has been carried out on the roll with the diameter $\varnothing$ 300 mm to verify the possible creation of the fourth surfacing. The basic material of the roll has been the steel labelled 24CrMoV55 - DIN 17240 with the good formability under the heat and machinable in the annealed or heat-treated state. It is suitable for the engine components strained in the higher temperatures. The chemical composition of the roll is shown in the table no. 1 and the mechanical properties in the Table no. 2. [6]

Table 1: Chemical composition of the steel 24CrMoV55 - DIN 17240 (in wt. %)

C	Cr	Mo	V	Mn	Si	P	S	Fe
0.20	1.30	0.35	0.55	0.5	0.30	0.022	0,015	Bal.

Table 2: The mechanical properties of the steel 24CrMoV55 - DIN 17240

Yield Strength (MPa)	Tensile Strength (MPa)	Elongation A5 (%)	Hardness [HB]
540	640-670	16	195-223

The roll assigned for the fourth renovation was firstly visually tested with focus on the crack presence on the body of the roll or in its cooling part. The roll did not give a sign of the trans-crystal cracks. [7] Consequently the worn-out roll was lathed with the diameter of 14 mm. After the turning, it was necessary to check the roll again, the surface of the roll was checked visually according to the norm EN 13018 and for the under-surface testing was used the ultrasonic method according to the norm EN ISO 11666. It was necessary to preheat the roll up to 200 °C during which the temperature must have been checked continuously even during the surfacing. The range of the surfacing temperatures was from max. 200°C up to 380°C (8).

For the renovation, the surfacing SAW technology was used, the cladding was made in three layers (10). The first bottom layer was created in the combination of the tubular wire UP-5-200-CZ $\varnothing$ 2.8mm and the addition F 56 with the aim of perfect connection of the basic material with the covering layer. The covering layers was made by combination of the wire UP-5-45-CZ $\varnothing$ 3,2 mm and the addition F 56. The parameters of the surfacing are presented in the Table no. 3. The chemical composition of the additional materials is displayed in the Table no. 4. For the surfacing the addition F 56 has been used whose basicity is 1.4 and the basic chemical composition is in the Table no. 5. [6]

Table 3: The parameters of the surfacing of the fourth cladding

Layer	Filler material	Diameter of wire [mm]	Cladding current [A]	Cladding voltage [V]	Cladding speed [m/h ¹]
First	UP-5-200-CZ	2.8	310	28	25
Covering	UP-5-45-CZ	3.2	390-450	30-32	25

Table 4: The basic chemical composition of the filler material (in wt. %)

DIN 8555	C	Mn	Si	Cr	Mo	Nb	N ₂
UP-5-200-CZ	0.05	0.8	0.6	16.5	-	-	-
UP-5-45-CZ	0.07	0.7	0.6	13.0	0.7	0.2	0.12

Table 5: The basic chemical composition of the addition F 56 (in wt. %) [6]

SiO ₂	MnO	Fe ₂ O ₃	Al ₂ O ₃	CaO	MgO
11-16	max. 1	max. 1	42-48	8-13	max. 1
CaF ₂	Na ₂ O	K ₂ O	BaF ₂	P	S
24-30	max. 0.5	max. 2.5	max. 1	max. 0.6	max. 0.6

Immediately after the surfacing it was necessary to temper the roll. The tempering temperature reached 540°C with the maximum heat speed 50 °C per hour and the residence to this temperature lasted for 6 hours. Subsequently the cooling of the roll was 40 °C per hour up to 210 °C followed by the free cooling in the air. [6.7]

After the surfacing and heat treating the roll has been chip machined with the diameter of $\varnothing$ 300h10 for the active part. Within the final testing of the surfacing the visual testing of the roll has been carried out according to the norm EN ISO 17637 as well as the penetration testing according to the norm EN ISO 23277 which has been supposed to reveal the surface and undersurface defects. For detecting the inner defects, the ultrasonic testing has been used according to the norm EN ISO 11666. Based on the NDT tests the roll has been classified as convenient.

After the successful surfacing creation, the destructive tests were done. To carry out the already mentioned tests it was necessary to take the example samples from the roll. In the Fig. 2 are shown the places where the samples for the destructive testing were taken. The samples from the cut roll have to be removed without the heat influence on the samples.

EDX analysis

For the EDX analysis the samples were taken from the covering layer and the observation was done with the microscope JEOL JSM-35CF. The EDX analysis itself was carried out on the analyzer LINK AN10/85S.

The metallographic analysis

On the cross cuts the macro and microstructure were evaluated according to the norm EN 1321. The examined samples were taken from the basic material (BM), the transition part and the surfacing metal. The samples were cast into the dentacryl, metallographically refined, polished and finally etched with the etcher Villela-Bain. The evaluation of microstructure was done with the light microscope Olympus TH4-200.

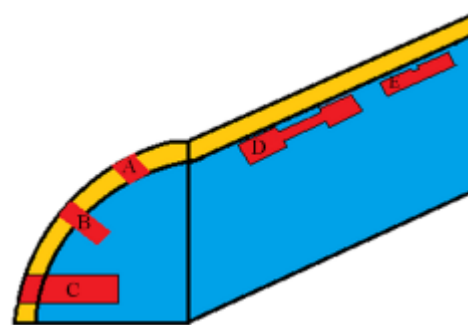


Fig. 2: The method of the sample taking [6]
(A – samples for the EDX analysis, B – samples for the metallographic analysis, C – samples for the hardness testing, D – samples for the tensile testing, E – samples for the impact testing)

The hardness testing HV

The hardness of the cladding, heat-affected zone (HAZ) and BM was realized on the cross cut of the roll according to the norm EN ISO 9015-1 using the Vickers' method and the engine HPO 250 with the load 100 N and the temperature 20°C and the indenter's operation lasted for 15 seconds. In the Fig. 3 the points of the incisions are depicted.

The tensile testing

The testing followed the norm EN ISO 6892-1. During the sample taking for the tensile testing the material were removed from the edge of the underclad layer, the Fig. 2 (D). The testing was carried out with the test engine TIRA test 2300 with the temperature 20°C. In the Fig. 4 is displayed the used example of the round shape.

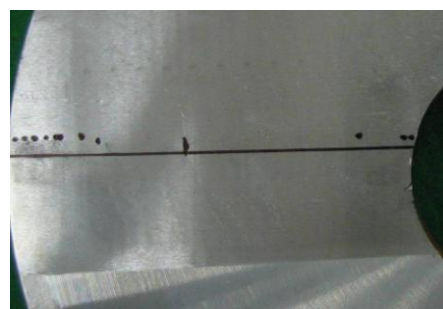


Fig. 3: The points of the incisions



Fig. 4: The sample for the tensile testing

3. Results

After the analysis of the cladding quality done by the visual, penetrant and ultrasonic method, the cladding of the roll was evaluated as convenient. Consequently, the destructive testing was carried out on the samples taken from the roll using the already mentioned method.

The chemical composition of the covering layer was identified by EDX analysis which is presented in the Table 6.

Table 6: Chemical composition of the covering cladding layer (in wt. %)

C	Cr	Mo	Ni	Nb	N ₂
0.05-0.07	12.5-13.5	0.7-1.1	3.5-4	max. 0.02	0.08-0.12

The macroscopic analysis

The macroscopic and microscopic structure was evaluated on the cross cuts of the roll. The macroscopic structure is seen in the Fig. 5. For better observation of HAZ it was necessary to etch the sample with the etcher Villela-Bain. The width of HAZ respects the amount of the input heat for the surfacing under the addition and duplicates the shape of the surfacing layers. In the macrostructure

the defects were not present. Martensitic microstructure of base material is in Fig.6.

The transition between the basic material and HAZ was fluent. By the influence of the added heat the transformation from the coarse texture bainitic forms to finegrained martensit was made. The place of mixture of the cladding with HAZ is narrow. The first layer of the clad metal is created by the coarse structure in the transit part. The microstructure of the welded layers is in the Fig. 7.

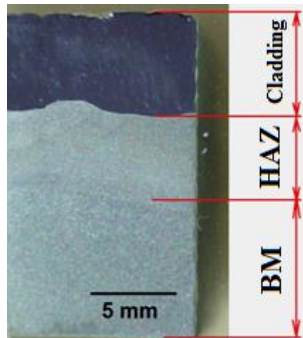


Fig. 5: The macrostructure of the cladding (BM – base material, HAZ - heat affected zone)

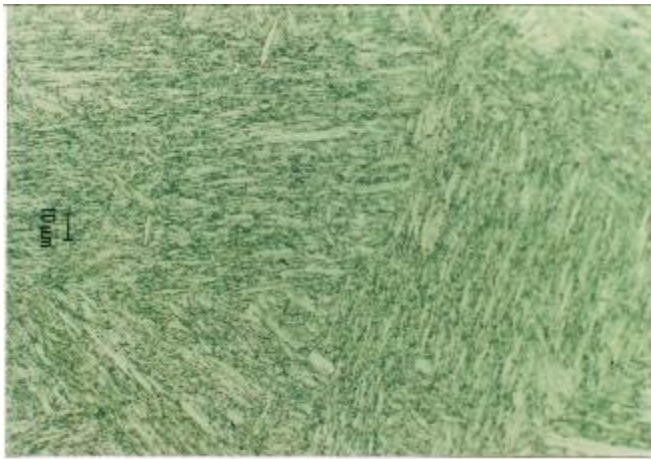


Fig. 6: The microstructure of the base material

The cladding is made of the martensitic structure where carbides parts are found. The interlayer has been made of the structure without strong lines of the grain's despite of the covering layer with intensive precipitates. While identifying, for more exact identification we have chosen the Schaeffler diagram.

Hardness testing HV

On the crosscut of the roll, the hardness of the cladding has been measured, HAZ and BM shown in the graph, on Fig. 8. So, the result is that the maximum average hardness was measured in the covering welded layer in the depth of 1 mm from the surface 405 HV10. Because of the growing distance of measuring from the surface, the decline of the hardness was depicted. In HAZ the average measured hardness was 258 HV10. The basic material was measured with the average hardness 247 HV10.

Tensile testing

From the results we can say that HAZ shows the average value Rm 939.4 MPa what refers to the increase of 42.3% compared to the heat non-influenced BM. Elongation (A5) has already been increased to the value of 17.3% compared to BM.

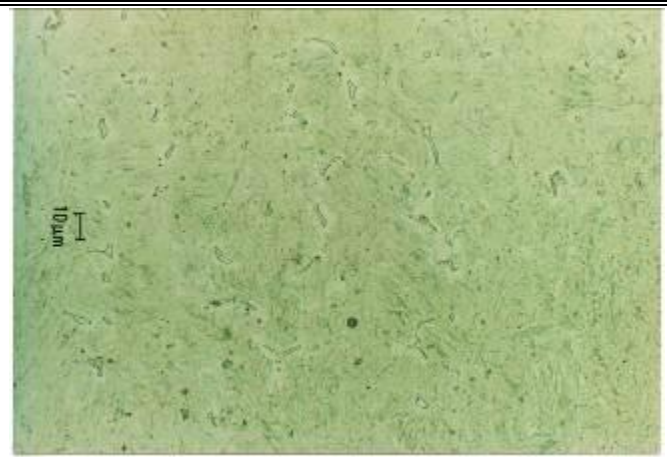


Fig. 7: Microstructure of the covering layer of the cladding

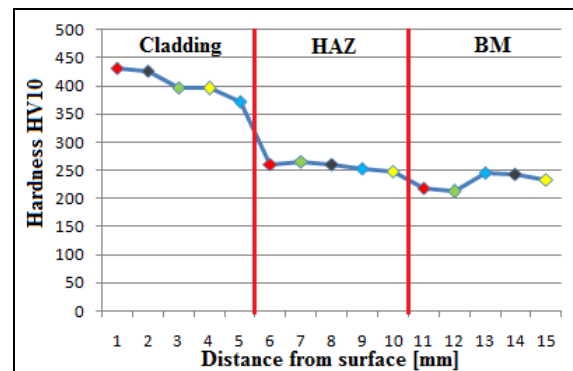


Fig. 8: Measured value of hardness

4. Conclusion

The article presents the results from the analysis of the welded layers on the roll of the continuous steel casting with the average $\phi 300$ mm from the material 24CrMoV55 – DIN 17420. The evaluated roll has been renovated by the technology SAW four times. The rolls of the continuous casting line are usually renovated 3-times maximum and then decapitated from the process of renovating the active plates. Because of the financial savings in the metallurgy, the possibility of the prolonging the operating life with one more cycle has been tested. The quality of the renovated roll has been evaluated by non-destructive and destructive testing. The visual, penetrant and ultrasonic testing of the welded roll has not confirmed the presence of the surface and under-surface defects. The destructive tests have been aimed on the analysis of the quality mainly in the heat influenced area which is the most defect sensitive. The defects found in this place are the most frequent reasons for the destruction of the welded layers on the rolls. The experiments have been carried out:

- the static tensile testing done according to EN ISO 6892-1 has confirmed the increase of the hardness material property in HAZ with the measured average values Tensile Strength = 939.4MPa, Yield Strength = 783 MPa and elongation A_5 = 17.3%.
- in the welds the metallographic analysis of the cross cuts has not identified the presence of the inner defects. The structure of the basic material of the roll is created by the low temperature martensite.

The structure of the interlayer and the covering layer has been formed by the low-carbon martensite. For increasing the resistance against the abrasive wearing the welded metal is alloyed with Cr and N whose main role is to strengthen the structure precipitally with carbides and nitrides.

This contribution has brought the useful information about the renovations of the continuous casting lines which are consequently applied in the operation of steel production using the continuous casting lines. Based on the experimental results we can state that the

evaluated roll fulfils the criteria of the renovation quality for reusing it in the continuous casting line.

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The practical applications of the concept of energy and technological compliance in materials science of polymer nanocomposites

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Abstract: The analysis of the mechanisms of implementation of the concept of multilevel modification in materials science and technology of polymer nanocomposites is carried out. It has been shown that the mechanisms of structure formation at the molecular, supramolecular and interfacial levels in nanocomposite materials based on industrial polymers of the class of polyamides, polyolefins, fluoroplastics modified by components that implement the nanostate phenomenon are based on:

– the formation of adsorption physical bonds in the boundary surface due to the energy interaction of active centers of nanosized particles with various shapes and components of the surface layer, which change the parameters of the rheological, stress-strain and adhesive characteristics of the composites;

– the demonstration of a structuring action by nanosized particles and components of the surface layer of particles, which manifests itself in the form of supramolecular and interphase ordering, physical compatibilization and non-chain stabilization, which increase the thermodynamic compatibility of the components of polymer-polymer and polymer-oligomer blends and inhibit thermo-oxidative and destructive processes in composites, causing a non-additive increase of the parameters of their stress-strain, adhesive and tribological characteristics.

KEYWORDS: NANOCOMPOSITES, POLYMER MATRICES, MULTILEVEL MODIFICATION, NANOSTATE, ENERGY AND TECHNOLOGICAL COMPLIANCE OF COMPONENTS

1. Introduction

Among the priority areas of the innovative strategy for the sustainable development of economic complexes of various levels is the practical implementation of the key component of convergent NBIC technologies – nanomaterials science and nanotechnology in order to increase the parameters of the characteristics of metal-polymer systems for various functional purposes.

In the nomenclature of modern engineering materials, a special place belongs to nanocomposites based on polymer, oligomeric and blend matrices, which, according to a number of parameters of functional characteristics, are uncontested materials in the production of motor transport, special, agricultural machinery, technological equipment, shut-off and control valves for heat power systems, petrochemical and processing industries. At the same time, an analysis of literary patent sources shows that the potential of industrial polymers in the creation of nanocomposites is not fully realized with a developed base of their large-tonnage production and equipment with modern technological equipment at the stages of obtaining and processing into products for various purposes. Therefore, the development of theoretical ideas about the mechanisms for the formation of the structure of nanocomposite materials based on industrially produced polymer and oligomeric matrices will make it possible to develop effective methodological approaches to the creation of domestic production of new generation composites in accordance with the needs of innovative enterprises.

The probability of the processes of formation of the structure of composite materials at different levels of organization is determined by the activation energy, which depends on the parameters of the energy characteristics of the components at a given technological impact. These parameters depend not only on the composition, but also on the dimensional and geometric features of material objects.

Studies of domestic and foreign experts have established the effect of the transition of a material particle upon reaching a certain size range into a state with special parameters of energy characteristics, called according to the established terminology a nanostate [1–4]. Obviously, the achievement of the nanostate by the component will have a significant impact on the structural processes in the composite material at different levels of organization, which determine the parameters of the stress-strain, tribological, adhesive and other characteristics of products in metal-polymer systems. At the same time, despite the experimentally established influence of energy parameters on structuring processes, there are no systemic studies of methodological approaches to the implementation of the nanostate phenomenon in materials science and the technology of nanocomposite materials based on industrial polymers. As a result, the achievement of synergistic effects of increasing the parameters of the performance characteristics of products from polymer

nanocomposites cannot be fully implemented in practical applications.

2. Methods of research

The main objects of study were nanodispersed particles of carbon-containing (graphite, DND, CNT, shungite, carbon fibers), metal-containing (oxides, salts of organic acids) and silicon-containing (mica, tripoli, opal, clay) compounds obtained by technological impacts on natural and synthetic semi-finished products produced at industrial enterprises in Belarus and the Russian Federation. Nanosized components were obtained by mechanical crushing and heat treatment of dispersed semi-finished products at temperatures of 673–1473 K.

Two main types of thermoplastic materials were used as polymer matrices. The first ones have hereditarily high viscosity (HHV) of the melt due to the chemical structure of the chain and molecular weight: polytetrafluoroethylene (PTFE) and super high-molecular polyethylene (SHMPE). The second group consisted of industrial thermoplastic polymers such as polyamide PA 6, high density polyethylene (HDPE), ethylene-vinyl acetate copolymers (EVAC), polypropylene (PP), thermoplastic polyurethane (TPU), etc. with characteristic parameters of rheological properties that changed upon the introduction of nanosized modifiers - acquired high viscosity (AHV).

Polymer materials were used in the state of industrial delivery in the form of granules or powder obtained by cryogenic dispersion of granules at a temperature of 87 K.

The structure and properties of nanocomposite materials and products produced from its were investigated using modern methods of physical and chemical analysis: IR spectroscopy (Specord), electron paramagnetic resonance (EPR) spectroscopy (RE 1306, Bruker), X-ray diffraction (Dron 2.0, Dron 3.0), differential thermal analyzes (Q-1500), optical (MIM-10, MF-2), scanning electron (ISM-50A, Nanolab-7) and atomic force (Nanotope III) microscopy. The energy state of nanoscale modifiers and composite materials was assessed from the EPR spectra and the spectra of thermally stimulated currents (TSC) on the original equipment of the V.A. Belyi Metal-Polymer Research Institute of National Academy of Sciences of Belarus (MPRI NASB). The dielectric characteristics of materials after energy exposure (laser, ion, temperature) were determined according to the appropriate standardized methods. The regulation of the nanorelief of the surface layer of polymer samples and fillers was carried out using a short-pulse laser and accelerated ion irradiation with a given power density.

The parameters of the stress-strain characteristics of the developed materials were evaluated on standard samples in accordance with the relevant standards (GOST). Tribological characteristics were

determined on universal or original friction machines (UMT, MI-2, SMC-2M, etc.) according to the "indenter – disk", "shaft – partial insert" schemes. Evaluation of the performance of products from the developed nanomaterials in the designs of automotive units for various purposes and technological equipment was carried out at the stands and in the process of virtual tests using the SKIF supercomputer and field tests. The test data processing was carried out by the methods of mathematical statistics using the standard software Microsoft Office 2020.

3. Results and discussion

When choosing modifiers for obtaining nanocomposite materials with optimized structural parameters that determine the feasibility and efficiency of their use in systems of a given functional purpose, we proceeded from the principle of energy and technological compliance of components based on the concept of reasonable sufficiency, taking into account technological, environmental and economic aspects [5–7]. Practical implementation of the developed methodological approaches ensures the achievement of technically significant effects of increasing the parameters of the stress-strain, adhesive, tribological characteristics of composites based on industrial matrices both with a doping content (0.001–1.0 wt. %) of modifiers and with its content of 20–40 wt. %. In this case, depending on the characteristics of the composition, structure, dispersion and shape of the modifying particles, various levels of structural organization are realized. For highly dispersed particles with a doping content (0.001–1.0 wt. %), The structure is mainly optimized at the supramolecular and intermolecular levels [8, 9]; when modifying matrices with active micrometer fragments (80–150 μm) of high modulus fibers (carbon, oxalane, glass) at a content of 5–40 wt. % the interfacial level plays a predominant role. In this case, modifiers can maintain the stability of the initial parameters of the characteristics during the formation of the composite and the operation of the product or metal-polymer system, or exhibit lability due to transformation under the influence of physicochemical processes, changing the initial structural parameters of the composite [10].

The mechanism of the structuring action of nanosized particles (NSP) in polymer and oligomeric matrices of various structures has been investigated. Based on the developed model, which assumes the formation of supramolecular spherical structures under the action of active centers of the nanoparticle, an analytical expression is obtained to calculate the concentration of the modifier sufficient to transfer the entire matrix to an ordered state.

As follows from [11, 12], the matrix will be completely modified provided that the modifier particle exhibits its activity in the boundary layer with thickness $L = r [1 + (\rho_f/\rho_p)] ((1/C_f) - 1)^{1/3}$, where r is the particle size; ρ_f, ρ_p – density of the filler and polymer; C_f – the content of the filler.

It follows from this expression that the parameter L is linearly related to the size of the nanoparticle and practically does not depend on the ratio ρ_f/ρ_p , which suggests similar mechanisms of the modifying action for particles of different composition and production technology. Even with a doping content (0.001–1.0 wt. %), The ratio $1/C_f \gg 1$ and the structuring effect of the nanoparticle on 2–3 adjacent layers of macromolecules provides a significant modification effect.

Experimental studies have confirmed the adequacy of this conclusion (Fig. 1).

It was found that the efficiency of the modifying action of a nanosized particle (NSP) is influenced not only by the size, composition, and structure, but also by its shape. From the analytical expression that determines the size parameter of a nanoparticle, characterized by a special energy state that affects the efficiency of the modifying action, $L_n = h \sqrt{3} \cdot \theta_D^{-1/2} / \sqrt{2m_e k}$, where h, k are the Planck and Boltzmann constants, respectively, m_e is the electron mass, θ_D is the Debye temperature, it follows its dependence on the crystal chemical direction [11, 12]. Therefore, using relatively large modifier particles, the surface layer of which contains nanosized components that satisfy the calculated L_n value,

it is possible to achieve technically significant modification effects using available technologies for the production and processing of polymer composites.

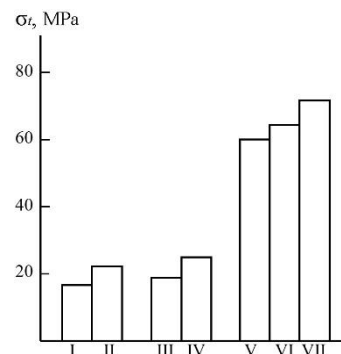


Fig. 1. Ultimate tensile strength σ_t for HDPE (I, II), PTFE (III, IV), PA 6 (V, VI, VII) of the original (I, III, V) and modified 0.05 wt. % DND (II, VII), Cu (VI) and 0.5 wt. % UPTFE (IV)

Model concepts of the mechanisms of modification of high-molecular-weight matrices by nanosized particles of various shapes have been developed. It is shown that the use of lamellar (scaly), whisker (fibrous) and spherical particles changes the degree of modification of the matrix M, which is determined by the ratio of the total modified volume to the total volume of the composite. Taking into account the different energy state of the NSP, determined by the parameter L_n , and taking into account the anisotropic nature of the Debye temperature θ_D , the ratio of the degree of modification by scaly (M_{sc}), whisker (M_{wh}) and spherical (M_{sph}) particles was obtained with the same content in the composite: $M_{sc} : M_{wh} : M_{sph} = 1 : 0,4 : 0,8$.

It follows from the obtained expression that when creating low-filled nanocomposites based on polymer matrices, it is preferable to use layered modifiers, which include natural silicates – clays, mica, talc, which, under certain conditions, are capable of dispersing with the formation of nanosized lamellar particles.

The carried out experimental and theoretical studies are based on the assumption that the structure, composition and shape of the NSP introduced into the polymer matrix remain unchanged. At the same time, there are classes of NSP (metal, oxide, metal-containing), which are capable of transforming as a result of physicochemical processes occurring in the boundary layers of composites under the action of operational factors (thermal, mechanical, mechanochemical, etc.) with the formation of products of another composition and structure with an excellent mechanism of structuring action on the matrix polymer. Therefore, a reasonable choice of NSP and technologies for its production for the implementation of targeted modification of a polymer or oligomeric matrix presupposes a systematic analysis of structural and phase transformations, taking into account the energetic and physicochemical aspects of the formation and functioning of a metal-polymer system within the framework of the concept of synergistic structuring, based on the proposed methodological principles for the implementation of the nanostate phenomenon. The developed model concepts of the influence of the energy and structural parameters of NSP on the efficiency of modification of polymer matrices made it possible to determine technological approaches to obtaining effective nanomodifiers using available semi-finished products in the form of layered minerals (clays, talc, mica, tripoli, etc.), as well as technological waste of chemical production (refined products of vegetable oils, phosphogypsum, products of metallurgical industries). The essence of the developed methods for the preparation of silicate-containing NSP consists in the thermal effect on dispersed particles of a semi-finished product obtained by dispersing in kinetic impact machine (crushers) with a temperature gradient of 800–1000 K in air or in a non-oxidizing gas flow with a density of $3 \cdot 10^6$ – $8 \cdot 10^7$ W/m². Intense thermal action leads to the destruction of the initial particles with the formation of nanosized fractions of various structures and compositions [12].

Preliminary modification of semi-finished products of layered minerals (clays, talc) with thermally decomposable compounds such as carbonates, formates, metal oxalates, organic refining products of vegetable oils, water-soluble polyamides increases the intensity of degradation processes by the stratification mechanism with the formation of lamellar particles. The developed methods make it possible to obtain effective modifiers of industrial thermoplastics with a size range of 10–30 nm and a long-term active state.

Implementation of the developed methods when modifying polymer matrices of NSP in an amount of 0.1–10.0 wt. % or diffusion treatment of products made of polymer composites based on industrial thermoplastics (aliphatic polyamides PA 6, PA 6.6, PA 11, polyolefins PP, HDPE) or its blends allows increasing the strength parameters by 1.1–1.3 times, wear resistance by 1.5–2.0 times, as well as resistance to the effects of thermo-oxidizing environments due to multilevel modification.

The developed principles of multilevel modification of composite materials, the formation of an integrated supramolecular structure by modifying the matrix with a set of nanosized particles by means of interfacial interaction catalysis make it possible to implement the concept of synergistic structuring in the preparation of nanocomposites based on thermoplastics, including those with increased melt viscosity (PTFE, SHMPE). An algorithm for the formation of compositions of high-strength wear-resistant composites based on high-viscosity matrices (PTFE, SHMPE), methods of their manufacture, providing an increase in the parameters of deformation-strength characteristics in comparison with analogs, has been developed (Fig. 2).

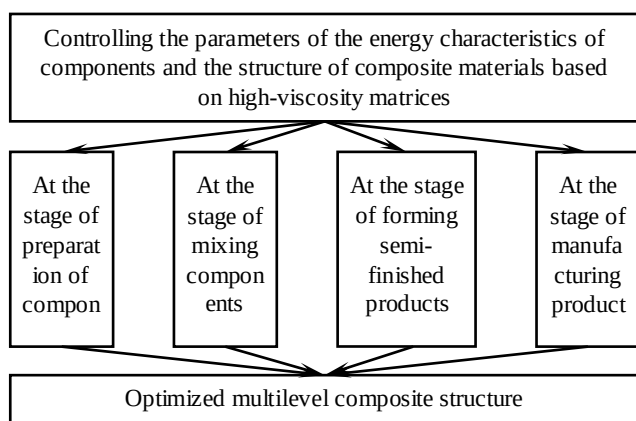


Fig. 2. Algorithm for the formation of a multilevel optimized structure of composite materials based on thermoplastic matrices with increased viscosity

When using nanosized modifiers (carbon black (CB), UPTFE, clay, talc), it is advisable to activate the components at the stages of preparation and mixing using energy (thermal, laser) impact. This approach was tested in the development of technologies for the production of low-filled (0.5–5.0 wt.%) nanocomposites using a combination of NSP (UPTFE, CB) and products of the activation of layered minerals by thermal action in the temperature range 473–1373 K. For the development of low-filled composites based on high-viscosity matrices (SHMPE, PTFE), options for implementing the principle of multilevel modification, based on a combination of components with different resistance to transformation under the influence of technological factors, have been proposed. Within the framework of the existing technological paradigm of fluorine composites, an imperfect structure is formed due to the absence of a pronounced viscous-fluid state of PTFE, which prevents the processes of monolithization and interphase interaction. The proposed combination of carbon-containing particles (CNT, CB) and UPTFE provides, due to the polymer-oligomeric structure and

special rheological characteristics, a decrease in structural heterogeneity, which favorably affects the parameters of the composite characteristics (Fig. 3). When dispersed particles of thermoplastics (polyamides, polyolefins, polysulfone) are used as modifiers under the influence of molding temperatures (573–623 K) for 8–24 hours, conditions are created for the formation of carbon-containing components with increased thermodynamic compatibility with PTFE, with a shape adapted to interparticle defects, and high parameters of stress-strain characteristics ($\sigma_t = 85\div90$ MPa).

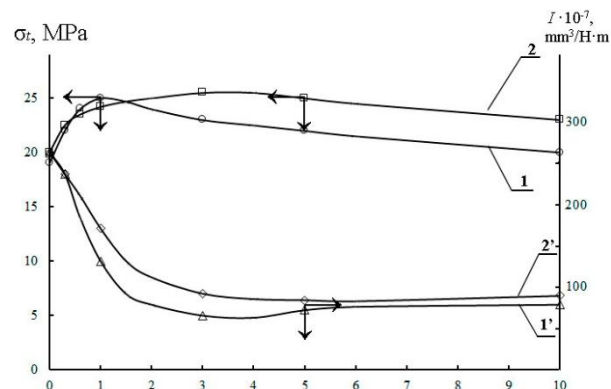


Fig. 3. Dependence of ultimate tensile strength (1, 2) and wear rate (1', 2') of composite materials based on polytetrafluoroethylene modified with ultrafine polytetrafluoroethylene (UPTFE) on the content of dispersed particles of carbon black CB P324 (1, 1') and CB P803 (2, 2'). The content of UPTFE in the composites is 2.0 wt. %

Dispersed particles of oligomers selected from the group of oligoimides (oligomaleimidoaminophenylene, oligomaleimidohydroxyphenylene, tetramaleimide, N, N'-bis-maleimides of unsaturated dicarboxylic acids, etc.) are an effective modifier of the transformable type. Carbonization processes under the influence of technological factors lead to the formation of carbon-containing particles with a nanoscale relief of the surface layer and high activity in the processes of interphase interaction, as a result of which structures with increased parameters of stress-strain ($\sigma_t = 36\text{--}46$ MPa) and tribological ($I \times 10^7 = 0.5\text{--}2.0$ mm³/N·m) characteristics.

When developing composites with a filler with a size range of 50–150 μm and a content of 10–35 wt. % the phenomenon of nanostate can be realized within the framework of the concept of energy and technological correspondence using mechanochemical activation.

Using the concepts of the mechanisms of structure formation of fluorine composites formed using mechanically activated components, developed by the scientific school of prof. Okhlopko A. A., methodological principles of fluorine composites technology are proposed, in which fragments of carbon fiber (CF) are used as a modifier (Fig. 4).

Activation of the components of composites based on PTFE, SHMPE at the stage of forming semi-finished products in accordance with patented technologies with the use of common equipment for cold monolithization followed by sintering made it possible to increase the ultimate tensile strength parameter for materials with CF content of 1–20 wt. % from 17–18 MPa to 20–35 MPa due to the provision of mechanochemical interaction at the “filler - matrix” interface due to the difference in the coefficients of thermal expansion.

The developed options for applications of the concept of energy and technological compliance are presented in table.

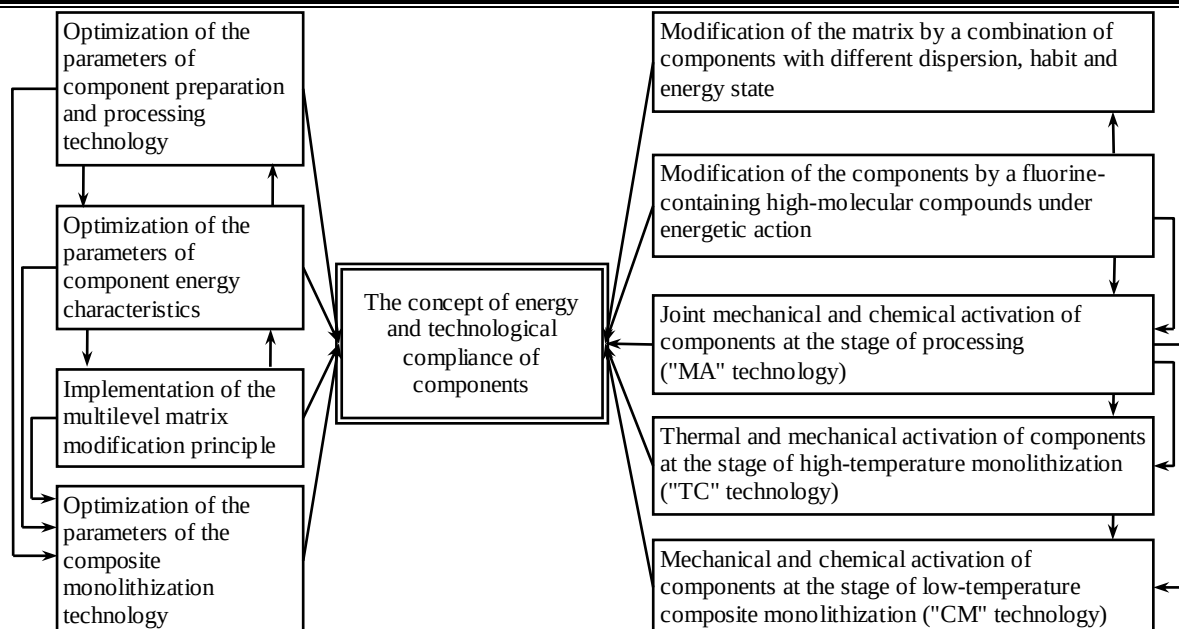


Fig. 4. Methodological principles of the technology of highly filled fluorine composites with increased performance parameters

Table. Practical applications of the concept of energy and technological compliance in materials science and technology of nanocomposites based on thermoplastics

Methodological principle of implementation	Developed material science and technological solution	Structural features of the nanocomposite and the achieved technical effects	The level of novelty of the developed solution
1	2	3	4
Physical compatibilization of blend components by nanoparticles	Introduction of nanosized particles under thermomechanical mixing of components	The formation of blend structure due to the formation of intermolecular bonds of the adsorption type. Increasing the parameters of stress-strain, tribological characteristics and resistance to thermal oxidative aging	BY patents for inventions No. 8674, 9215, 9820, 9397, 10585, 10986, 17434. RU patents for inventions No. 2265037, 2266988, 2268273, 2276677, 2278875, 2283325, 2305117, 2309964.
The principle of multilevel modification of the composite material matrix	Introduction of a set of modifying particles with different size parameters, energy activity and shape	Formation of an integrated structure with intermolecular, supramolecular and interfacial components. Increasing the parameters of stress-strain characteristics and wear resistance	BY patents for inventions No. 8480, 11421, 21061.
Mechanochemical activation of components at various stages of the technological process	Mechanochemical action on components in kinetic impact or friction-type machines at the stages of preparation, mixing of components, processing of products (semi-finished products)	Formation of products with nonstoichiometric composition due to intermolecular and interphase interaction of components, a decrease in the number of structural defects, an increase in thermodynamic compatibility. Increasing the parameters of the stress-strain characteristics of products	BY patents for inventions No. 8480, 9396, 14813, 17180, 17719, 18089, 21059, 21060, 21061, 21397, 21900. RU patents for inventions No. 2266925, 2266988.
The use of crystal chemical parameters of dispersed modifiers for structuring matrices at various levels of organization	Thermal, thermomechanical, laser, ionizing effects on a semi-finished product in the form of microparticles, fibers, films to obtain nanoscale fractions or nanorelief of the surface layer	Structuring a matrix with a high level of ordering at various levels of organization under the influence of the nanostate factor of disperse particles or relief components. Increasing the parameters of stress-strain, adhesive, tribological characteristics of products and coatings	BY patents for inventions No. 8999, 10391, 10795, 10901, 10898, 11382, 11694, 17248, 17719, 18063, 22316. RU patents for inventions No. 2269554, 2332524, 2332525, 2307855, 2321603, 2329285, 2338764. UZ patent for invention No. 06365.
Inhibition of the processes of corrosion and mechanical wear by separating layers of nanocomposite materials	Introduction to the friction contact zone of carbon-containing, silicate-containing particles in combination with oligomeric and polymer components and oils	Formation of a nanostructured separating layer in the contact interaction zone with low resistance to tangential shear and the ability to signal-alternating transfer	BY patents for inventions No. 7832, 8470, 18073. RU patents for inventions No. 2243998, 2248389.

1	2	3	4
Recovery of the structural potential of regenerated thermoplastics by doping modification with nanosized particles	Modification of regenerated thermoplastic matrices with a doping amount of nanosized particles (0.001–0.1 wt. %) in the process of thermomechanical action on the melt	Formation of a predominantly spherulite structure of the matrix polymer with the participation of radical fragments of aging and thermal mechanical destruction. Increasing the parameters of stress-strain characteristics and resistance to service life of products	BY patents for inventions No. 9820, 10586. BY patents for utility models No. 11240, 11241, 11264, 11265, 11266, 11630, 11631, 11634, 11635, 11773, 11776, 11882, 11967. RU patents for inventions No. 2283325, 2305117, 2309964. RU patent for utility model No. 170525.

The comprehensive studies of the directions of the practical implementation of the nanostate phenomenon in materials science and the technology of nanocomposites based on industrial thermoplastics have confirmed their validity and adequacy to a functioning industrial enterprises.

4. Conclusion

Methodological principles have been developed for the implementation of the nanostate phenomenon in material science and technology of functional nanocomposites based on industrial thermoplastics of the class of polyolefins, polyamides, fluoroplastics by optimizing the structure at the intermolecular, supramolecular and interfacial levels, ensuring the achievement of a synergistic combination of performance parameters based on:

- established crystal-chemical prerequisites for the selection of natural and synthetic carbon-containing, metal-containing and silicon-containing semi-finished products for the directed formation of active nanosized particles with given structural, morphological and energy parameters under optimal technological (mechanochemical, thermal, laser) impact;
- the implementation of the conditions for the energy compliance of nanomodifiers with the dominant mechanism for the formation of the optimal structure of polymer, oligomer and blend matrices at various levels of organization – molecular, supramolecular and interfacial;
- ensuring the conditions for the manifestation of the preferred mechanisms of interphase physical and chemical interactions of components with the formation of boundary layers with optimal structure, which determine the mechanisms of destruction of nanocomposites under the influence of various operational factors.

The physical and chemical aspects of the modifying effect of nanoparticles of various compositions and structures in thermoplastic matrices are considered. The features that determine the activity of low-size particles in the processes of transformation of the structure of the binder composite material at the molecular, intermolecular and supramolecular levels, consisting in their special energy state, due to the habit, size of the factor and the production technology, have been established. Using the proposed analytical expression, the analysis of the size factor determining the nanostate of NSP of mono- and polyatomic substances, which determine its transition to the nanostate with increased modifying activity to high-molecular matrices, has been carried out.

The features of the mechanism of the modifying action of nanoparticles of various production technologies, composition and structure are considered. It is shown that the most important criterion of activity in the processes of adsorption interaction of a nanoparticle with macromolecules of a polymer or oligomer matrix is its energy state, characterized by the presence of an uncompensated charge with a long relaxation time.

Variants of practical application of the concept of energy and technological compliance in materials science and technology of nanocomposites based on industrial thermoplastics have been developed.

5. Acknowledgements

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A new blood storage refrigerator design for ATEX Directive

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Abstract: Blood storage refrigerators are one of the indispensable products of the medical sector. Blood storage refrigerators are produced in various capacities and per different blood components. Although there are commercial refrigerators with various features among our company's products, we do not have a blood storage refrigerator for the medical sector. Although there are a few companies that manufacture blood storage cabinets in our country, there is no company that fulfills high-security requirements per the ATEX Directive (2014/34/EU). In the field of an industrial kitchen, our various international competitors develop blood storage refrigerators and offer them to the market as a product with high added value compared to industrial refrigerators. Innovative blood storage refrigerator, which meets the safety requirements by the ATEX Directive for the first time in our country with studies based on R&D systematics, is a prototype that can compete and commercialize with international products in the medical field, after testing and evaluating it with its original design and prototype developed.

Our prototype is designed to meet high safety requirements according to the ATEX directive (2014/34/EU). The innovative blood storage refrigerator meets the safety requirements of the ATEX directive. Simulation of the cooling process of the innovative prototype is made together in cooperation with a local university. In contrast to our commercial refrigerators, we meet the refrigeration, hygiene, health, and safety requirements of the original blood storage refrigerator prototype, which meets with all international standards for the medical device sector (EN 60079-0, EN 60079-15, etc.) and ATEX directive (2014/34/EU).

Keywords: BLOOD STORAGE REFRIGERATORS, ATEX DIRECTIVE AND SAFETY REQUIREMENTS, REFRIGERATION TECHNOLOGY

1. Introduction

Blood storage refrigerators stand out as critical products that are used to preserve blood and its products in hospitals and blood centers at certain times and temperatures. Over 100 million blood units are collected worldwide each year [1]. Although there are commercial refrigerators with various features among our company's products, we do not have a blood storage refrigerator product for the medical sector. Although there are a few companies that manufacture blood storage cabinets in our country, there is no company that fulfills high-security requirements under the ATEX Directive (2014/34/EU).

In the sector of the commercial kitchen, our various international competitors develop blood storage refrigerators and offer them to the market as a product with high added value compared to commercial refrigerators.

Innovative blood storage refrigerator, which meets the safety requirements under the ATEX Directive for the first time in our country with studies based on R&D systematics, is a prototype that can compete and commercialize with international products in the medical field, after testing and evaluating it with its original design and prototype developed.

The blood that is used without any treatment after it is taken from the donor is called whole blood. It is mainly used as a source for the preparation of blood components. The temperatures of the storage conditions vary according to the differences in various blood components. The storage temperature for whole blood is +4°C [2-6].

There are very few studies on innovative blood storage refrigerator applications that meet the safety requirements for the medical sector by the ATEX Directive. The main reason for this is that these products are commercial.

The average global Research & Development investment rate (R&D spending as a percentage of sales) is estimated to be around 8% in the medical technology sector [7].

In 2020, more than 14,200 patent applications were filed with the European Patent Office (EPO) in the field of medical technology representing a 2.6% growth in patent applications

compared to the previous year [8]. Patents in the field of medical technology climbed to the top in 2020 (Fig. 1).

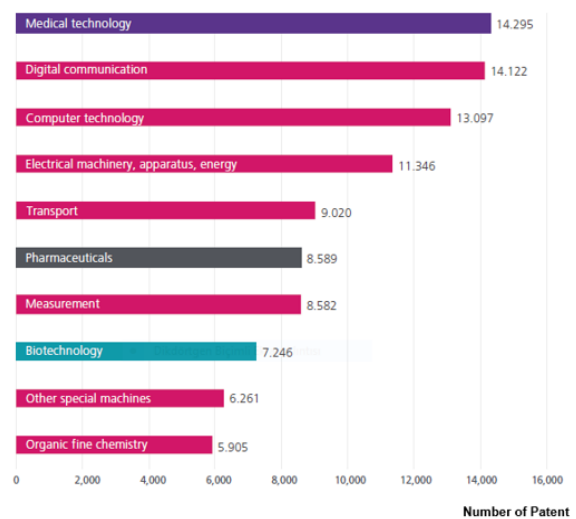


Fig. 1 Number of patent applications filed with EPO, 2020 [8].

The Japanese research group detected ammonia, lactate, pH of the preserved blood by sensing the temperature of the material and its surface in the cooling system they developed for whole blood protection. and analyzed ATP levels [9].

The project activities of obtaining the innovative blood storage refrigerator by the ATEX Directive (2014/34/EU) for the first time in our country through R&D studies were carried out in line with international standards (EN 60079-0, EN 60079-15 etc.).

2. Methodology

The design validation data (the placement of blood units according to the original designs, the cooling performance evaluations according to the air circulation and temperature distributions, etc.) made important contributions before the prototype fabrication.

The cooling system hardware and the placement of the shelves are provided specifically to the design of the innovative blood storage refrigerator prototype. The main body of the innovative prototype is made of stainless steel (AISI 304) material. Polyurethane printing was carried out between the stainless steel material for insulation purposes.

The innovative prototype has an audible and visual warning system against the door being left open for a long time and/or forgetting to close the door. In addition, there is a lock system to prevent it from being used by unauthorized personnel. Double glass is used in the door of the innovative prototype to maintain the temperature inside the cabin.

A front view of the innovative blood storage refrigerator prototype is given in Fig. 2.



Fig. 2 Front view of the innovative blood storage refrigerator prototype.

Images of the temperature data recording system and warning system of the innovative blood storage refrigerator prototype, which meets the safety requirements for the medical sector by the ATEX Directive, are given in Fig. 3.

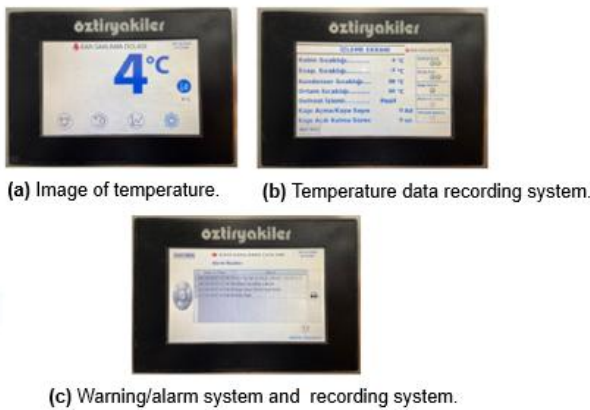


Fig. 3 Images of the temperature data recording system and warning system of the innovative blood storage refrigerator prototype.

The images of the blood storage bags (450 ml.) used in the testing and evaluation phase of the innovative blood storage refrigerator prototype that meets the safety requirements for the medical sector by the ATEX Directive are given in Fig. 4 and Fig. 5.



Fig. 4 (a) Image of blood storage unit packed, (b) Blood storage unit (450 ml).

Gross capacity 500 Lt. of innovative blood storage refrigerator prototype and 250 blood units (450 ml/piece) capacity (Fig. 5).



Fig. 5 Placement of blood units (450 ml/piece) inside the innovative prototype.

3. Experimental procedure

After the design validation studies of the innovative blood storage refrigerator, prototype manufacturing and assembly stages were completed. The innovative prototype includes 5 different blood storage shelves and an inner door made of plexiglass material is placed in front of each shelf so that the temperature distribution between the shelves is not adversely affected when the outer door is opened.

Simulation studies and design validation studies were carried out to ensure that the innovative blood storage refrigerator prototype provides effective cooling specific to the design. In the testing and evaluation phase, glycerol was used instead of whole blood.

In the work on the innovative prototype, ATEX directive (2014/34/EU) and EN 60079-0, EN 60079-15 etc. related to the medical equipment sector. standards were used. It has been determined that the innovative prototype is suitable for Zone 2 according to the ATEX directive. In addition, IIB (gas group) and T2-T6 (temperature) are valid for the innovative blood storage refrigerator prototype.

In the innovative blood storage refrigerator prototype, which meets high safety requirements by the ATEX Directive (2014/34/EU) for the first time in our country in the medical sector, whole blood storage is provided at $+4^{\circ}\text{C} (\pm 1.5^{\circ}\text{C})$, (Fig. 6).

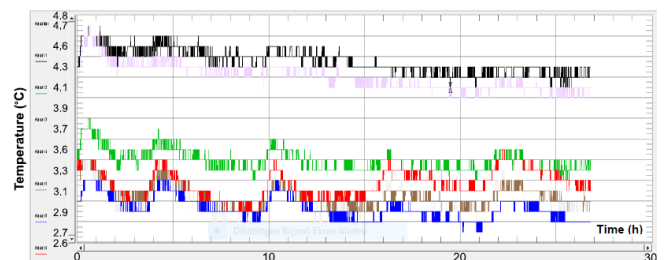


Fig. 6 The cooling performance of the innovative blood storage refrigerator prototype is at $+4^{\circ}\text{C} (\pm 1.5^{\circ}\text{C})$.

At least 15% energy saving (1,071 kWh/day) was achieved in the energy consumption value of the innovative blood storage refrigerator prototype, which meets high safety requirements by the ATEX Directive (2014/34/EU) for the medical sector (Fig. 7).

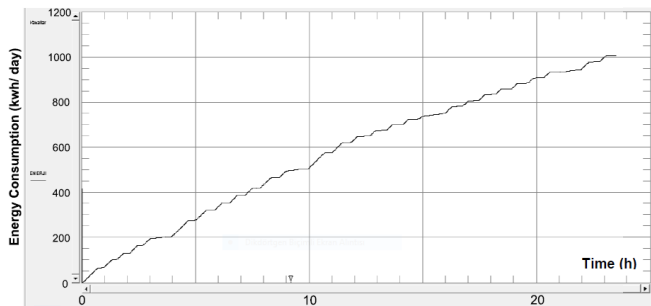


Fig. 7 Energy consumption of the innovative blood storage refrigerator prototype.

The noise level measurement value (53.6 dBA) during the working process of the innovative blood storage refrigerator prototype is given in Fig. 8.



Fig. 8 The noise level measurement value of the innovative blood storage refrigerator prototype.

With the R&D activities, for the first time in our country, unlike our commercial refrigerators, the uniquely designed blood storage refrigerator prototype, which operates by the international standards of the medical device sector and the ATEX Directive (2014/34/EU), provides the cooling, hygiene, health and safety requirements at a high level with R&D gains.

In this context, it has been achieved to obtain an innovative prototype by making use of the effective operation of the innovative prototype, engineering calculations obtained during the design verification phase, simulation data (air circulation in the cooler chamber and temperature distributions, etc.) and test and analysis data.

4. Conclusions

Following the R&D studies on the innovative blood storage refrigerator prototype, the following outputs were achieved;

It has been achieved to meet the high safety requirements of the innovative blood storage refrigerator prototype with the ATEX Directive (2014/34/EU) compared to the standard domestic blood storage refrigerators in our country, with studies based on R&D systematics in the medical device sector.

In the innovative blood storage refrigerator prototype, which meets the high safety requirements in the medical sector by the ATEX Directive (2014/34/EU), whole blood storage has been achieved at +4°C (±1.5°C).

The design-specific innovative blood storage refrigerator prototype has been provided with a gross 500 Liter and 250 blood units (450 ml/piece).

In the innovative blood storage refrigerator prototype, which meets the high safety requirements in the medical sector by the ATEX Directive (2014/34/EU), the energy consumption value has been at least 15% energy saving (1,071 kWh/day) compared to the imported similar product.

The innovative blood storage refrigerator, which meets the safety requirements by the ATEX Directive for the first time in our country with studies based on R&D systematics, has been tested and evaluated with the original design and prototype production. A prototype that can be commercialized in the medical field has been developed with the cooperation of industry-university.

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Impact analysis of kinetics and dynamics of SO₂ and NO_x adsorption from flue gases on the geometry of the column with a fixed carbon bed

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Abstract: The purpose of this research paper is to analyse the impact of kinetics and dynamics of sulphur dioxide (IV) and nitric oxide (II) adsorption from the flue gases on the geometry of a column with a fixed carbon bed. Using the following kinetics equation: pseudo-first and pseudo-second-order, Webber-Morris and Elovich and dynamics Langmuir equation, essential operation parameters for activated carbon made from coconut shell modified by copper have been found. Comparison of two schemes (simultaneous adsorption of SO₂ and NO after CO₂ adsorption and simultaneous adsorption of SO₂, NO and CO₂) has been done to determine the adsorption's time, efficiency and a breakthrough curve. Process scaling has been used to evaluate the chances of adsorption flue gas treatment implementation in industrial production. Bed height has been modelled considering the flow of fuel gases for ½ technical scale and flow of fuel gases for large combustion plants. Match factors values have pointed that the research is more accurate for NO_x than SO₂ adsorption regardless of the operation scenario. To reduce the height of one column, a battery of columns should be applied, e.g. for NO adsorption in one segment and SO₂ adsorption in another segment.

KEYWORDS: SO₂ ADSORPTION, NO_x ADSORPTION, FLUE GASES PURIFICATION, FIXED CARBON BED, ISOTHERMS, MATHEMATICAL MODELLING

1. Introduction

SO₂ and NO_x in flue gases are the main air pollutants. Such gaseous substances affect human health and the environment badly. For many years have International Directives have been created to limit the emissions of these gases. Adsorption distinguishes it from general flue gases treatment methods. Although adsorption efficiency is lower compared to the main BAT techniques, the simplicity of the installation, ability to implement into existing boiler systems and low exploitation cost due to the activated carbon from waste usage are strong advantages. Activated carbon has a large specific surface area and a highly developed structure in a wide range of pores. It may be an ideal pollutant adsorbent with strong adsorption performance and great chemical stability [1].

Activated carbons are made from a variety of starting materials. Bio-waste is often used for the production of activated carbons due to the huge amount generated each year [2]. The most commonly used are palm shell, palm stone and coconut shell. It happens because palm and coconut bio-wastes have a large amount of micropores and macropores. It makes the possibility of selecting raw materials to produce activated carbon with certain pore size distribution at the beginning of the process. This allows reducing production costs at the carbonization stage. To design an adsorption process and apparatus under large combustion plants conditions, to scale up the process is a need to model kinetics and dynamics. It is impossible to check the behaviour of adsorbents under all possible conditions on a laboratory scale.

2. Prerequisites and means for solving the problem

2.1 Kinetic and dynamics modelling

The model research were performed using the Langmuir model in the case of the adsorption dynamics analysis and the pseudo-first-order, the pseudo-second-order, the Weber-Morris and the Elovich models in the case of adsorption kinetics analysis. A brief description of each of them is presented below.

Langmuir model

Process dynamics calculations have based on the Langmuir isotherm equation. This is the simplest model which leads to uncomplicated mathematics. The model assumes constant adsorption energy that is independent of the surface coverage and adsorption is a monolayer. The following form of the equation has been used in modelling [3]:

$$q = q_m \frac{b \cdot C}{1 + b \cdot C}; \text{ where } b = \frac{k_{ads}}{k_{des}} \quad (1)$$

Where C is the initial concentration of the adsorbate [mol/g], q is the adsorption capacity of adsorbent [g/kg], q_m is Langmuir constant related to adsorption capacity [g/kg] and b is Langmuir constant related to the rate of adsorption [m³/kg].

Pseudo-first-order model

The pseudo-first-order (PFO) model is formed as irreversible first-order kinetics. PFO model assumes that the adsorption process can be regarded as a first-order reaction due to the presence of the amount of adsorption at equilibrium [4]:

$$\ln(q_e - q) = \ln q_e - k_1 \cdot t \quad (2)$$

Where q is the adsorption capacity of adsorbent [g/kg], q_e is amount of adsorption at equilibrium [g/kg], t is time [s] and k₁ is PFO reaction rate constant [1/s].

Pseudo-second-order model

The pseudo-second-order (PSO) model assumes that the adsorption process can be regarded as a second-order reaction towards the difference between the amount of the actual adsorbate and the adsorbate in the equilibrium state. The transformed form of the equation is presented below [5]:

$$\frac{t}{q} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e} \quad (3)$$

Where q is the adsorption capacity of adsorbent in time [g/kg], q_e is amount of adsorption at equilibrium [g/kg], t is time [s] and k₂ is PSO reaction rate constant [s·g/kg].

Weber and Morris model

Weber and Morris (WM) equation is well known as the diffusional model. This model assumes that the diffusion in the micropore is the rate-limiting step. To determine the initial adsorption behaviour, the following equation is deduced [6]:

$$q = k_{WM} \cdot t^{1/2} + A \quad (4)$$

Where q is the adsorption capacity of the adsorbent [g/kg], t is time [s] and k_{WM} is Weber-Morris reaction rate constant [g/kg·t^{1/2}]. The presence of the A constant is explained by the external mass transfer which is insufficient.

Elovich model

The Elovich (E) equation has been suggested as the best available procedure for describing the kinetics of chemisorption. This equation assumes that the reaction takes place at the heterogeneous surface. The high value of the match factor of the model adsorption curve compared to experimental data indicates that the reaction rate is limited by chemisorption. Elovich equation is expressed as [7]:

$$q = \frac{1}{\beta} \cdot \ln(t) + \frac{1}{\beta} \cdot \ln(\alpha \cdot \beta) \quad (5)$$

Where α [g/kg·s] and β [g/kg] are constants during any of experiments, t is time [s] and q is the adsorption capacity of adsorbent [g/kg].

Model validation

Parameter S has been used to evaluate which model most accurately describes the adsorption process. It is the sum of squared differences of model and experimental adsorption capacity. The equation is expressed as:

$$S = \sum_{i=1}^n (q_{mod} - q)^2 \quad (6)$$

2.2 Process scaling

The computational model is based on mass transfer zone theory. The assumptions are: idealized plug flow, convective mass transfer, constant gas feed velocity through the bed and constant temperature of the process. Another assumption is that adsorption capacity in time t divided by the concentration in time t equals initial adsorption capacity divided by initial concentration ($\frac{q}{C} = \frac{q_0}{C_0}$). Also, if the concentration in any time t is equal to $\frac{1}{2}$ of the initial concentration we get the half-time $t_{1/2}$. This half time is essential for scaling up. Due to the knowledge of the mass transfer zone theory and Langmuir isotherm, it is possible to determine the equation:

$$t = t_{1/2} + \frac{\rho_b q_m}{K a C_0} \left[\ln 2x - \frac{1}{1 + b C_0} \ln 2(1 - x) \right] \quad (7)$$

Where t is time [s], $t_{1/2}$ is half-time [s], ρ_b is volumetric density [kg/m³], q_m is the maximum adsorption capacity of an adsorbent [mg/g], Ka is mass transfer constant [1/min], C_0 is the initial concentration of SO₂ or NO in feed [mg/g] and x is defined as C/C_0 where C is the concentration of SO₂ or NO at the time t .

The equation describing the adsorption duration time emerges from the mass balance of the adsorbent bed. The equation is expressed as:

$$t = \frac{q_m \cdot \rho_b \cdot H}{w \cdot (C_0 - C)} \quad (8)$$

Where t is time [s], ρ_b is volumetric density [kg/m³], q_m is the maximum adsorption capacity of an adsorbent [mg/g], C_0 is initial concentration of SO₂ or NO [mg/g], C is concentration of SO₂ or NO at the time t [mg/g] and w is feed velocity [m/s].

2.1 Research material

The matter of this article is activated carbon made from coconut shells modified by copper (CU-SAC) [8]. Table 1 presents the parameters characterizing its porous structure.

Table 1 Porous structure parameters of Cu-SAC (based on [1])

Sample	Value
Total volume [cm ³ /g]	0,623
Surface area [m ² /g]	1,339
Micropore volume [cm ³ /g]	0,544
Average pore width [nm]	1,860
Volumetric density [kg/m ³]	680,0

Model studies were performed for SO₂ and NO adsorption from the stream which was previously purified of CO₂ (first scenario) and for simultaneous adsorption of SO₂, NO and CO₂ from the flue gases (second scenario). The flue gases composition for the first operation scenario is: 94,7 % N₂, 5% O₂, 2000 ppm SO₂, 1000 ppm NO. Composition for the second scenario: 84,7 % N₂, 5% O₂, 10% CO₂, 2000 ppm SO₂, 1000 ppm NO. The feed flow through the reactor has been fixed at 400 ml/min. The reaction temperature has been preset to 323 K and the pressure to 1013 hPa. The adsorption capacities for SO₂ and NO for both scenarios were borrowed from the work [8]. The reason for choosing the experimental data from the indicated literature was the convergence of the composition of the simulated flue gases with the real flue gases [9], with particular emphasis on the concentration of SO₂ and NO. This approach made it possible to scale the model data for the needs of the deposit height assessment.

3. Results of discussion

As mentioned before, modelling has been conducted for two scenarios basing on experimental data from the source article [8]. In the first scenario, the first step is CO₂ adsorption out of flue gases (which is not the subject of model research for this article). The second stage is about simultaneous adsorption of SO₂ and NO from a CO₂-free stream. Initial concentration of SO₂ in mixture is 2000 ppm=3,12·10⁻⁵ [mol/g], while initial concentration of NO is 1000 ppm=3,33·10⁻⁵ [mol/g]. Maximum adsorption capacity q_m of SO₂ has been measured when outlet to inlet concentration ratio equals 0,82 and analogous NO ratio equals 1.

SO₂ kinetics model research has proved that both Weber-Morris and Elovich equations predict the reaction's behaviour alike. It means that under designed conditions both chemisorption and diffusion in micropores were limiting stages of the process. In this case, pseudo-first and pseudo-second equations are not included because their match factor (parameter S) has occurred to be too low. Experimental data with breakthrough curves are presented in Fig. 1.

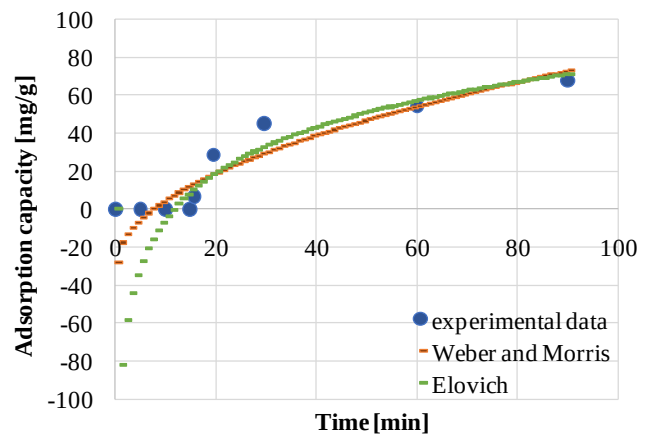


Fig. 1 Adsorption breakthrough curves for SO₂ on Cu-SAC – first scenario

For the first scenario, modelling of kinetics adsorption of NO has been described successfully with pseudo-first and pseudo-second-order equations. Although adsorption test points have been almost immaculately matched by the pseudo-second-order model, this model has not predicted a situation when there is overproduction of NO before 20 minutes of measurement. Elovich and Weber-Morris equations describe the adsorption process precisely when the changes of concentrations are rapid. Previous models cannot describe the process with high accuracy when the reaction rate decreases. Same as for SO₂ both chemisorption and diffusion in micropores seem to be limiting steps of the adsorption

process of NO. Experimental data with breakthrough curves are presented in Fig. 2.

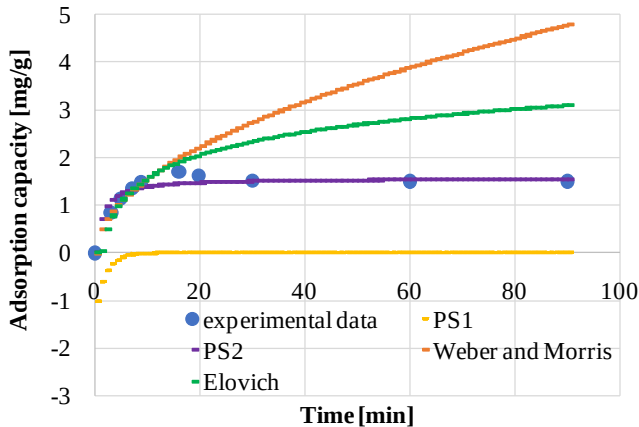


Fig. 2 Adsorption breakthrough curves for NO on Cu-SAC – first scenario

The second scenario is about simultaneous adsorption of SO₂, NO and CO₂ from the flue gases. However, CO₂ adsorption is not of interest to this article. As can be seen in Fig. 3 and 4, test points have similar values to those from the first scenario. There are also the same initial concentrations. The only difference is between values of maximum adsorption capacities. Every breakthrough curves observation in the second scenario has led to the same conclusion as in scenario one.

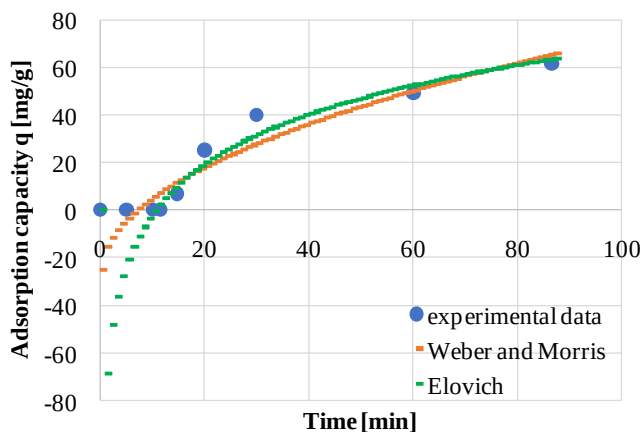


Fig. 3 Adsorption breakthrough curves for SO₂ on Cu-SAC – second scenario

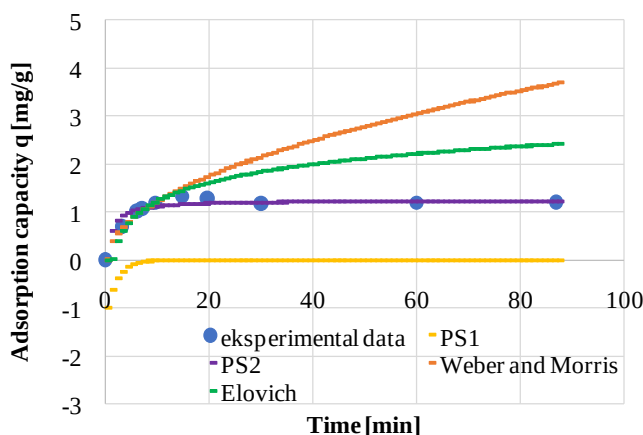


Fig. 4 Adsorption breakthrough curves for NO on Cu-SAC – second scenario

Both scenarios have resulted in identical conclusions. The second scenario confirms the fact that both chemisorption and

diffusion in micropores were limiting steps of the process. Also in both scenarios, the maximum adsorption capacity of SO₂ (for ratio C/C₀=1) has been not achieved. It is believed that it could have been due to by the co-adsorption of other pollution. In the first and second scenarios overproduction of NO has been registered, which could be related to the co-adsorption of SO₂ [1].

To sum up, experimental values of adsorption capacity for the scenario one are: q_{SO₂}=67,91 mg/g, q_{NO}=1,50 mg/g; and for scenario two: q_{SO₂}=61,50 mg/g, q_{NO}=1,20 mg/g.

Lower values of the S parameter are achieved for the Elovich equation (Tab. 2). It proves that chemisorption influences limiting reaction rate more than diffusion in micropores. Although the differences are not too significant.

Table 2 Values of S [g²·kg⁻²] parameter – first (1) and second (2) scenario for SO₂ and NO

	SO ₂		NO			
	WM	E	PFO	PSO	WM	E
1	548	359	20	0,19	16	5,23
2	295	137	13	0,10	10	3,09

Mass transfer zone theory, which has been presented in section 2.2, enables us to figure the half-process time. It is possible because of the graphic solution of the Langmuir equation using the MS Excel Reglinp function. The figured value of t_{1/2} is a model time for the adsorption process that can be used for rescaling laboratory column to the industrial conditions. The bed height remains unknown, however, it can be calculated from the transformed equation number 8:

$$H = \frac{t \cdot w \cdot (C_0 - C)}{q_m \cdot \rho_b} \quad (9)$$

Where t is time [s], w is feed velocity [m/h], ρ_b is volumetric density [kg/m³], q_m is the maximum adsorption capacity of an adsorbent [mg/g], C₀ is initial concentration of SO₂ or NO [mg/g].

The geometry of the column used in the experiment is 240 mm in height and 18 mm in diameter (the d/H ratio is equal to 0,075). Table 3 and Table 4 contain essential data for calculations (time, feed velocity, initial concentration of SO₂ or NO, concentration of SO₂ or NO at any time t, maximum adsorption capacity of an adsorbent) and calculation results (height, diameter and diameter to height ratio).

Concentration C has been chosen from Fig. 1, 2, 3 or 4 (depending on the scenario and type of pollution) for the first test point greater than zero. As long as the adsorption capacity measurement point obtains zero, the fixed bed removes pollution with maximum efficiency. The t value in Tables 3 and 4 informs how long maximum efficiency happens. The best operating point of the fixed bed occurs when the active sites are not yet occupied by contaminant particles. The time is long enough to guarantee the stream to be purified from SO₂. This conclusion is related to obtaining 4 measuring points at the zero value for adsorption capacity, which means that the stream is continuously purified with 100% efficiency. In the case of NO, it is a much shorter process due to the unfavourable process temperature. To extend NO adsorption, a higher process temperature would have to be used or the modification of the surface of the Cu-SAC would have to be changed. However, this could lead to the deterioration in SO₂ adsorption.

Basing on the source article [10], which is about the plant of the Bergbau-Forschung process for flue gases desulphurization, it has been chosen to use two volumetric flow rates i.e. 100 m³/h as the flow of fuel gases for ½ technical scale and 10 000 m³/h as the flow of fuel gases for large combustion plants. Knowing the values of the

flow rates, the gas flow velocities necessary for further calculations were figured.

Table 3 Input data for scaling up calculation – first (1) and (2) scenario for SO₂

Type of scenario	1a	1b	1c	1d
t [s]	4080			
w [m/h]	23,58	3,2	56,89	261,34
C ₀ [g/m ³]	2,13			
C [g/m ³]	0,21			
q [g/kg]	67,91			
H [m]	3,99	0,54	9,57	44,20
d [m]	0,018	0,040	0,75	3,49
d/H	0,005	0,074	0,078	0,079
Type of scenario	2a	2b	2c	2d
t [s]	5160			
w [m/h]	23,58	2,53	46,21	207,15
C ₀ [g/m ³]	2,21			
C [g/m ³]	0,24			
q [g/kg]	61,50			
H [m]	5,72	0,61	11,2	50,22
d [m]	0,018	0,055	0,83	3,92
d/H	0,003	0,077	0,074	0,078

Table 4 Input data for scaling up calculation – first (1) and (2) second scenario for NO

Type of scenario	1a	1b	1c	1d
t [s]	206			
w [m/h]	23,58	4,50	85,54	391,89
C ₀ [g/m ³]	1,06			
C [g/m ³]	0,59			
q [g/kg]	1,50			
H [m]	2,25	0,43	8,17	37,43
d [m]	0,018	0,041	0,61	2,85
d/H	0,008	0,076	0,075	0,076
Type of scenario	2a	2b	2c	2d
t [s]	186			
w [m/h]	23,58	4,30	80,20	365,77
C ₀ [g/m ³]	1,1			
C [g/m ³]	0,64			
q [g/kg]	1,20			
H [m]	2,47	0,45	8,41	38,35
d [m]	0,018	0,035	0,63	2,95
d/H	0,007	0,077	0,075	0,077

The computation data are given in Tables 3 and 4 (time, feed velocity, initial concentration of SO₂ or NO, the concentration of SO₂ or NO, adsorption capacity). Also, the results (height, diameter, height to diameter ratio) are given there. Four scenarios have been determined: a - bed height calculated for feed velocity and diameter (both specified in [2]); b - bed height calculated for feed velocity specified in [2]; c - bed height calculated for the volumetric gas flow rate of 100 m³/h; d - bed height calculated for the volumetric gas flow rate of 10 000 m³/h. In scenarios a, b and c the diameter has been changed to obtain a height to diameter ratio of about 0,075.

The ratio of the column diameter from the source article [2] to the calculated height was much less than 0,075 in cases of both SO₂ and NO. The large height of the column with such a small diameter suggests two solutions. One of them is the construction of a battery of adsorption columns to separate the height over several apparatuses. The second one is a selection of the optimal column diameter to obtain the d/H ratio close to the value of 0,075. It has been decided to use the second solution. Variants b, c and d show

what real dimensions of the column would have been if we had chosen the 0,075 ratios (like a reference value). Tables 3 and 4 suggest that the apparatuses would be too big. With such large sizes of heights and diameters, it is worth dividing one big column into a column battery. That would enable an operation at different temperatures. Then, a low-temperature process, which enhances the adsorption of SO₂, can be executed in one column, while in the next column a high-temperature process improving NO adsorption can be performed.

3. Conclusion

The adsorption characteristics of SO₂ and NO on activated carbon impregnated Cu have been investigated. Basing on data modelling can be concluded that the adsorption of SO₂ and NO (in parallel) can be precisely described by the Langmuir isotherm, by the Weber-Morris equation and Elovich equation, while for NO adsorption only the pseudo-first-order and pseudo-second-order equations are sufficiently accurate. The rate of adsorption of both SO₂ and NO is primarily limited by chemisorption, but diffusion in the micropores also has a significant impact. The NO adsorption capacity is much lower than the SO₂ adsorption capacity. This is due to the preparation of activated carbon, the process conditions and the impregnation with copper which promotes the adsorption of SO₂ rather than NO. Referring to model data, to reduce the height of the column, a battery of columns should be used instead. This solution would provide the possibility of using other carbon materials and other process parameters depending on the segment, i.e. for NO adsorption in one and SO₂ adsorption in another segment. It would have a positive effect on the efficiency of flue gas purification by the adsorption.

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Investigation of rubber granules used in artificial turf systems with FTIR spectroscopy with ATR system and DSC

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Abstract: The purpose of this study was to investigate the structure of recycled tires which are used in artificial turf/ grass as infill materials. One of the most important issues, especially in Albania is proving that these materials are recycled. In this paper it is presented the FTR with ATR system methods analyses. That will provide info regarding the combining material in rubber granules, for the investigation of their structure, it was used the spectroscopy method, with vibration infrared and Fourier FTIR transformation equipped with ATR system, a method which enables analysis of samples of thick surface, without any prior preparation. The scanning of samples was done with wavelength from 4000-400 cm⁻¹. At the same time was possible to see the changes in the micro-structure of the tires by using the Differential scanning calorimetry (DSC) analyses.

Keywords: T Synthetic Rubber, FTIR-ATR, DSC, Structural Investigation

1. Introduction

The rubber industry began when Charles Goodyear invented the first usable mixed rubber: natural rubber plus sulfur. The concept of mixing rubber materials to improve the performance is still of primary importance today [1]

Rubber can be produced both naturally, through the latex found in certain plants; and synthetically, through a process that uses unsaturated hydrocarbons. In addition, rubber is a polymeric material widely used in the automotive industry. Flexibility and stability are the most characteristic features of this material. Chemical construction and physical state of rubber depends on carbon bond which can be coiled or complex. The high elasticity of rubber depends on the ability of these connections to organize and pull. Due to the extreme prevalence of rubber products the tires are discarded and rubber recycling has become more common [2].

Rubber can be recycled using one of three basic methods: by reusing (retreading old tires produces functional refurbished tires). By burning; tires produces energy used for different purposes [1]. By chopping down and forming an entirely new product, such as playground surfacing or using them directly as infill material especially in artificial turf. This group of recycled rubbers will be the focus of our study.

By using rubber particles in applications such as soccer fields offers several benefits, including decreasing and sports injuries. Advantages in artificial terrain lie in rubber ability to withstand aggravated climatic conditions, even during or immediately after a rain storm [2].

The granulated rubbers used as infill material for artificial turf are recycled mostly from the tires of cars and trucks [3]. These tires are supposed to be abrasion resistance, aging resistance, temperature resistance, resistance to oxygen and chemicals therefore are added fillers like carbon black during vulcanization with sulfur [4-5]. As such it is very important to know what kind of additives they have. Therefore, the purpose of this paper is to investigate the components of granulated rubbers used in artificial turf. The samples are randomly chosen from different fields and for investigations are used two different test methods; the Infra-Red spectroscopy by Fourier Transform FT-IR ATR and Differential Scanning Calorimetry (DSC).

2. EXPERIMENT Materials and Methods

For this study are taken into account eight granulated rubbers from different football fields that are used as fillers in artificial grass football fields, received by Albanian and foreign market. In table 1 are summarized the detailed prescription of the samples, stating color, shape and size.

Table 1: Studying rubber sample

The first equipment used to test the samples is Spectrometer Bruker Tensor 27, equipped with Platinum ATR, enabling the analysis of thin samples without any prior preparation. Instrument resolution was 4cm⁻¹. Wave number interval was measured from 370 to 4000cm⁻¹. Number of accumulations to reduce the noise was 10. For structural analyses and filler identification was used OPUS software and previous literature conducted on rubbers.

Sample	G-1	G-2	G-3	G-4	G-5	G-6	G-7	G-8
Color	White	Green	Black	Black	Black	Black	Black	Black
Shape	Granule 2.5mm	Granule 0.8mm	Granule 0.8mm	Granule 0.8mm	Granule 0.8mm	Granule 2.0mm	Granule 1.1mm	Granule Fine

The principle of this is FTIR technique is that light introduced into a suitable prism at an angle exceeding the critical angle for internal reflection develops an evanescent wave (a special type of electromagnetic radiation) at the reflecting surface. Interaction of this evanescent wave with the sample determines ATR spectrum recording. Infrared (IR) spectroscopy is a very important non-destructive technique for identifying the chemical bonds in unknown compounds. This information is important for qualitative as well as quantitative determination of the chemical compounds. DSC measures the heat flow into or from a sample as it is heated, cooled and/or held isothermally. The technique provides valuable information on softening temperatures (or T_g), melting temperatures, heats of melting, percent crystallinities, and re-crystallization (temperatures and heats) [6, 7-8]. In order to determine the thermal properties, we use Differential Scanning Calorimetry (DSC). The chosen temperature range for testing the rubber is from -80 0C to +200 0C with cool/heat step of 10 0C/min. The equipment used is DSC 200 F3Maia (costumer laboratory) rate of 10 C/min in a nitrogen environment.

The sample mass is between 3.5 and 4.5 mg, which is low enough to avoid problems caused by heat and material transfer. Samples are heated from 40 to 2000C at a heating rate of 10 K/min⁻¹ using

nitrogen as purging gas at a flow rate of 40 ml/min. The experiments are carried out in air atmosphere. Two pans are heated in the measurement chamber.

3. Results and Discussions

The received spectrum, presented respectively for the tested samples, is a two-dimensional plot in which the axes are represented by intensity and frequency of sample absorption. The frequencies are helpful for the identification of the sample's chemical make-up due to the fact that chemical functional groups are responsible for the absorption of radiation at different frequencies. The concentration of component can be determined based on the intensity of the absorption.

For the first sample of rubber, named G-1, the two main component seem to be Polystyrene butadiene ABA Block (28% Styryne) Kraton D 1101 presented with the molecular formula $(C_4H_6)_x (C_8H_8)_n$, and Rubber carbon filled. The identification and the molecular formula are found directly from the library of the OPUS software.

Per each sample the spectra is accompanied by the name of the compound of the presented elements (see figure 2 to 3).

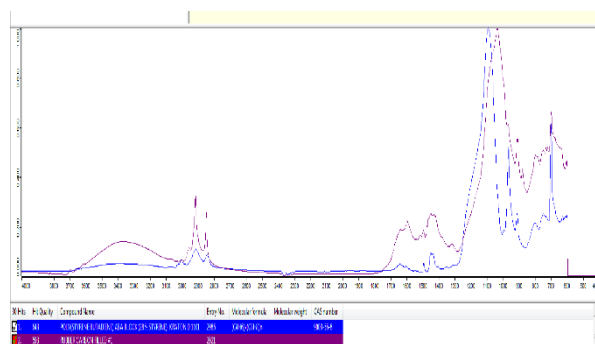


Fig. 2 IR spectrum of artificial rubber G-1

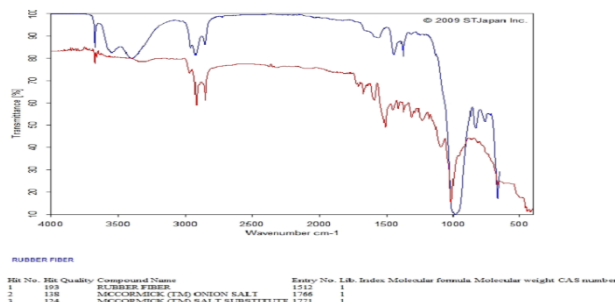


Fig. 3 IR spectrum of artificial rubber G-2.

In all spectra's we identify the presence of rubber as basic material. Groups of curves of spectra in the wavelength range 2850 -3000 cm^{-1} resulting from links absorptions of C-H3, C-H2 and C-H during deformation. Curves group with wavelengths 2150 - 2300 cm^{-1} is attributed to absorption of C = C bonds, as in C = C bonds attributed to the peaks frequencies of wave number 1500-1600 cm^{-1} . During analyzing and comparing the spectra library of software Opus was noted the presence of glass fibers as the main filler. Small differences in wavelengths of spectra are attributed to the presence of different fillers in rubbers. The greatest impact in fillers is the intensity of peaks, as well as their duplication.

By using the program was possible to calculate the characteristics of each curve for first second heating and cooling down.

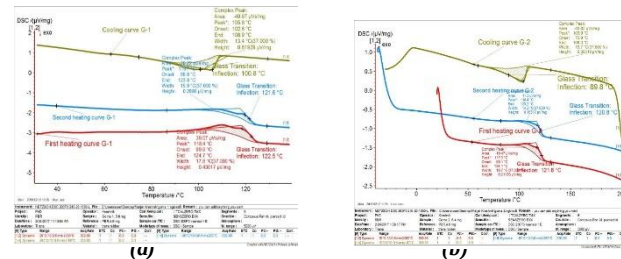


Fig 1: DSC curves of first, second heating and cooling down, for sample G-1. (a), DSC curves of first, second heating and cooling down, for sample G-2

As can be seen from the figure 1 and 2, (for sample G-1 and G-2), the graph show a slight difference in the shape of the curves, between first and second heating, respectively for sample G-1 and G-2. Thus by influencing also on the heat capacity, but not influencing the melting temperatures, which show almost the same value. The melting characteristics of the tested rubbers, for the first and the second heat, show different values, as expected. The different types of recycled rubber will have different properties regarding the specific heat capacity and melting temperatures and this reflects the differences due to thermal history. The melting characteristics of the tested rubbers, for the first and the second heat, show different values, as expected. Interesting is the fact that same samples show higher values of second melting heat, this could be interpreted as a result of re-crystallization of the product see the fig.2. From the segment analyses, of the first heating, it is possible to find glass transition, melting temperature and to calculate the total heat flow of melting.

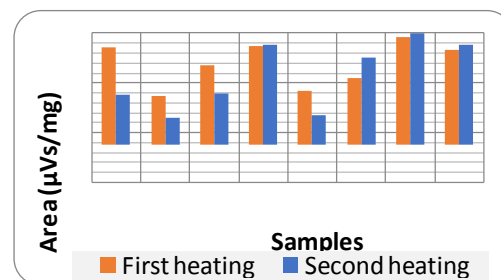


Fig 2. Graphically presented the comparison of the heat capacity of all the tested samples, in first and second heating.

4. CONCLUSION

The present paper aims to investigate the structure and the content of recycled tires used in artificial turf/ grass as infill materials. Structural investigation involved vibration spectroscopy with infrared Fourier transformation FTIR-ATR Method with DSC. Analyzes of the received spectra helped identify rubber as a basic element in all the tested samples. In addition, efforts were made to identify the fillers used for strengthening the physical-mechanical properties of the rubber. The low intensity of peaks shown in spectra made the identification of fillers difficult. This technique provides information on the chemical structure and this is achieved with a small amount of material. The combination of the FTIR-ATR Method with DSC is used to distinguish similar materials, and those materials that have the same temperature. Tg depends on the morphology of the rubber particles, which is influenced by the processing conditions and its thermal history. Observing higher values of heat capacity in the second heating, compared to the first heating. This can be explained by the presence of various additives that can be recrystallized, however this needs a more detailed analysis which is in further research work.

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