



# **Eurasian Journal**

# Of

# **Environmental Research (EJERE)**

Volume 1, Issue 2

1 December 2017

www.cessciencegroup.com





# **EDITORIAL BOARD**

**Editor-in-Chief** 

Assoc. Prof. Dr. Serkan SAHINKAYA

# **Editors**

Prof. Dr. Magdalena BALINTOVA (Technical University of Kosice, Slovakia)

Prof. Dr. Maria A. MIMIKOU (National Technical University of Athens, Greece)

Prof. Dr. Yiannis MATSINOS (University of the Aegean, Greece)

Assoc. Prof. Dr. Bilal TUNCSIPER (Omer Halis Demir University, Turkey)

Assoc. Prof. Dr. Iwona SKOCZKO (Bialystok University of Technology, Poland)

Assoc. Prof. Dr. Levent ALTAS (Aksaray University, Turkey)

Assist. Prof. Dr. Ahmet AYGUN (Bursa Technical University, Turkey)

Assist. Prof. Dr. Ece Ummu DEVECI (Omer Halisdemir Universitesi, Turkey)

Assist. Prof. Dr. Hakan DULKADIROGLU (Nevsehir Haci Bektas Veli University, Turkey)

Assist. Prof. Dr. Huseyin CUCE (Nevsehir Haci Bektas Veli University, Turkey)

Dr. Muhammed Kamil ODEN (Selcuk University, Turkey)

Mag. Neşen ERTUGRUL, M.A. (Alpen-Adria University, Austria)

# EURASIAN JOURNAL OF ENVIRONMENTAL RESEARCH (EJERE)

# CONTENTS

Title of Articles	Page Numbers
Application Potential of Gasification Technologies in Rural Settlement	1 – 7
Areas	
Multicriteria Analysis for Flood Vulnerable Areas in Southeastern Slovakia	8 - 19
Comperatively Investigation Pretreatments of H <sub>2</sub> SO <sub>4</sub> and Ultrasound	20 - 30
Effect for Corncob to Increase Available Bioenergy Potential by Response	
Surface Methodology	

# **Application Potential of Gasification Technologies in Rural Settlement Areas**

# E.Ü. Deveci<sup>1</sup> and Ç. Gönen<sup>\*1</sup>

<sup>1</sup>Department of Environmental Engineering, Nigde Ömer Halisdemir University, Nigde, Turkey. (Corresponding Author's E-mail: cagdas.gonen@gmail.com)

#### ABSTRACT

The rural settlement area of Niğde Çukurkuyu was chosen as a model location in this study to support rural development and sustainability. In order to identify the feasibility of the technology; the population, energy consumption, available potential raw materials (household and agricultural waste amount depending on years) of the settlement have been determined and analyzed and an economic feasibility report has been prepared. According to the obtained data from the region, 30% of the agricultural land is used and annual average of generated agricultural waste is 32200 tons. Depending on the season, averagely 1080 tons of domestic waste potential is available at the settlement. According to these data, estimated installed power of the gasification/plasma gasification plant which use of household waste can be 3 MW. The planting of energy plants such as Switchgrass and Sweet sorghum into unused agricultural land can increase the installed power of the plant to up to 18.8 MW. 1.1% of the energy produced by the process can meet the electricity needs of a 1000 selected rural residential area. Plus, entire heating requirement of the site can be met by 35% of the energy of process. With the remaining energy generated can be used by the grid, so the national economy will be contributed. Finally, it is obviously that a significant energy potential is available for rural development and sustainable energy production

**Keywords**: Climate change mitigation, energy plants, renewable energy, rural life, waste management.

## **INTRODUCTION**

World energy demand has been increased as parallel to population growth. Although urban area has higher demand to energy compared to rural areas, rural areas' energy demand is crucial for daily life, agricultural and livestock activities, which are farmers' main income. The context of Turkey's energy demand is as similar as other countries. Turkey's 80% of energy is outsourced; besides Turkey has a high-energy potential because it is an agricultural country. Though Turkey has various energy production plants, almost all of them cause environmental problems such as carbon dioxide emission or waste heat. On the other hand, Turkey has significant amount of renewable energy sources such as wind power, solar power or biomass energy. Even though biomass energy, such as municipal solid waste (MSW) or agricultural waste (AW), does not have widespread applications, electricity production from biomass can support the gap of fluctuation occurred the solar power and wind power sources (Öztürk, 2002; Ertürk et. al., 2006).

Since the technological revolution, the importance of energy security has increased dramatically because industrial production demands energy supply continuously. That's why developed and under developed countries are in competition, due to the energy and energy security are crucial and indispensable part of sustainable development. In order to reach sustainable development, sustainable energy production must be completed. That's why fossil

fuel based energy sources have shifted to renewable sources, otherwise environment, which is the one the important element of the sustainably concept, could be destroyed (Seydioğulları, 2013).

Nowadays, the greatest impact on the environment is greenhouse gas emission, which could be prevented by the renewable energy sources such as solar power, wind power, biomass, geothermal etc. This context gives an ignition to improvement and investment to renewable energy technologies. In developed countries, biomass utilization in industry is highly improved. Although, the ratio of the biomass energy decreased to 3%, it is clear that the bioenergy utilization has important situation for many countries such as Finland, Sweden, and the USA whose biomass ratios are 15%, 9% and 4% respectively (Koç & Garip, 2008; The World Energy Council, 2016).

According to biomass gasification models, the efficient operation of a biomass gasifier depends on a number of complex chemical reactions, including fast pyrolysis, partial oxidation of pyrolysis products, gasification of the resulting char, conversion of tar and lower hydrocarbons, and the water-gas shift reaction. These complicated processes, coupled with the sensitivity of the product distribution to the rate of heating and residence time in the reactor, required the development of mathematical models. The main goals of these models are to study the thermochemical processes during the gasification of the biomass and to evaluate the influence of the main input variables, such as moisture content, air/fuel ratio, producer-gas composition and the calorific value of the producer gas (Arnava et. al., 2010). Recently, waste to energy technology development has increased rapidly. Especially, gasification and plasma gasification technologies are the promising ones. These technologies have higher efficiency capabilities than the other conventional systems and they are much suitable to utilize in and dispose the medical, municipal and agricultural wastes. All kind of raw materials that are derived from carbon base, have applied with the system. By gasification systems, the carbon-based-raw materials are converted to heat energy via partially oxidation process. Gasification generally has four steps, which are drying, piroliz, oxidation and reduction. There are some other kinds of gasification processes that have been used however; fluidized bed and plasma gasification is the most common types. Their some significant advantages are low emission, low amount of final inert material, usable by-products and low greenhouse gas footprint. In the Table 1.1 below, the content of the compounds after the gasification process is given (Klein, 2002).

Sulphur	< 200 ppmw
Alkali metals	< 1 ppmw
Valitile metals	1 ppmw
Halogens	1 ppmw
Particle	< 20 ppmw

**Table 1.1.** Syngas content after treatment process in gasification process (Marano, 2013).

Gasification processes produce slag as a by-product, which is an inert material that does not create any contamination to the soil or water. Plus, it can be used as an aggregate on concrete production. An example of slag content is given at Table 1.2.

Compaund	Unit	Amount
Arsenic	mg/L	< 0.001
Cadmium	mg/L	< 0.001
Chrome VI	mg/L	< 0.005
Chrome VI	mg/L	< 0.001
Mercury	mg/L	< 0.0001
Selenium	mg/L	< 0.001

Table 1.2. Slag content from gasification plant (Marano, 2013).

In this study, to investigate sustainability of rural areas and solid waste management, Çukurkuyu town was chosen as a study area. Projected gasification plant can be utilized for solid wastes, agricultural wastes and medical wastes. Waste management and renewable energy production is indispensable part of the sustainability issue especially for rural areas. Çukurkuyu is a rural town and municipal solid waste and agricultural wastes are regularly produced at this town. In this study, energy potential of solid wastes was investigated. Plus, uncontrolled  $CO_2$  emission from solid waste had prevented. Besides, thanks to energy from solid wastes  $CO_2$  have been saved from the fossil fuels.

# MATERIAL AND METHODS

# Çukurkuyu town

Çukurkuyu is a town of Bor district at Niğde province. The town is at 37°52'N 34°20'E, it is situated in the plains of Central Anatolia. The distance between Bor and Çukurkuyu is 25 km and from Niğde city center to Çukurkuyu is 35 km. Çukurkuyu town has 7300 hectare unused agricultural field and 9800 hectare field which belong to Ministry of Treasury. Although household number of the Çukurkuyu is almost 1000, only 600 homes have permanent residents. Other 400 residents have used only summer season for a short time.

# Çukurkuyu town energy consumptions

All houses are separate private house at the Çukurkuyu town. Permanently residence 600 house are consumed mid quality coal to heating purpose during winter season. Electricity consumption of Niğde province is equal to Turkey average consumption ratio which is 2565 KWH/year.person. But according to "Turkish Statistical Institute" the daily electricity consumption of one house is averagely 10 KWH/day and electricity consumption values of Çukurkuyu town is compatible with this standard value.

# *Çukurkuyu town agricultural data and numbers*

Population of Çukurkuyu is 2367 and main economic income of the local people is agricultural activities which are livestock and farming activities. Especially sugar beet, tomatoes, apple, corn and water melon is primary agricultural products. The amount of agricultural products and their amount of seasonal wastes values are shown in the Table 2.1. As shown in Table 2.1. the ratio of agricultural waste are high because of unexpected frost weather or hail fail.

Product	Decares/ year	Ton waste / year
Melon, Watermelon	6000	21000
Tomatoes	5000	10000
Sugar beat	1200	1200
Corn	1000	250

Table 2.1. The amount of agricultural products and their waste

Nowadays cattle number have rose to over 7000 and the number of sheep and goat have reached over 9000. All animals are separated uniformly to the village area. This town is the highest number of animals compared to the population than the other towns of Bor.

## Çukurkuyu town municipal solid waste amount

Although the amount of municipal solid waste can be seasonal fluctuations, averagely 1080 ton waste have been produces from town and then these solid waste have transferred to landfill area which is far away over 45 km from the town.

# **RESULTS AND DISCUSSION**

# Gasification Plant Estimation with Municipal Solid Wastes and Agricultural Wastes

The annual amount of MSW and agricultural wastes are 1080 and 32450 tons respectively. However, available waste amount from the region is up to 33530 tons per year as explained. For the calculation of the plant parameters, the studies from Tolay (2011) is used as references. While daily raw material amount is 91.86 T/day, expected syngas production amount is 5000Nm<sup>3</sup>/h which is equal to 3688 GJ/year. That means to 3.3 MW installed capacity, if the plant is run 8000 hours per year. The plant consumes 10% of the produced energy. For thermal energy calculations, gasification plant can produce 6MW thermal energy but 50% of it should be used for internal purposes.

Electricity Fed-in tariff of Turkey is 0.133 \$/kw, if energy is coming from renewable sources. As a result, the annual income of the electricity would be equal to 3192000 \$. On the other side, some expenditure are indispensable. They are agricultural waste transfer from field to plant, some additional fuel for plant maintenance, official payments and salaries. If they are calculated, roughly they would cost 217500\$, 218000\$, 33000\$, 17000\$ and 390000\$ respectively. Total amount of expenditure is about 617.000\$. So, expected annual net profit would be almost 2600000\$. The assumed first investment cost is approximately 10000000\$ in which details are given at the Table 3.1.

Unit	Price	Unit	Price
Fuel accept, Storage and Feed	150000\$	Syngas Compressors	450000\$
<b>Biomass Drying Units</b>	250000\$	Waste Heat Storage	300000\$
Gasification Reactor	1100000\$	Gas Turbine and Gas Engine	1500000\$
<b>Oxygen Production Unit</b>	500000\$	Steam turbine	500000\$
Syngas Cleaning	1000000\$	Power Building	150000\$
Syngas Pipe System	150000\$	Support Systems And Emission Control Systems	600000\$
Pipes and Valves	50000\$	Electric Systems	800000\$
Thermal Isolation and Personal Protection	50000\$	Installation	110000\$
Ash Storage and transfer system	50000\$	Licenses and Engineering	750000\$
PLC System	100000\$	TOTAL	9550000\$

**Table 3.1.** Economic indicators of the gasification plant.

# Gasification Plant Estimation with Energy Plants

If the 8550 ha area, which is equal to 50% of public land, in the town were used for energy plant growing and assuming annual yield would be roughly 6-25 ton/ha plus, the amount would be averagely up to 200000 tons per year. According the report from Soylu (2009), the amount of dry matter per hectare is 12.8 tons and total amount is 109440 ton. The calculations showed that the installed capacity is almost 18.80 MW, that's equal to 150400 MWH electricity energy per year. Moreover, although 50% of it has to be utilize by the process, 320000 MWH excess thermal energy can be produced from the system.

The hourly feed stock needed for the system is 12.60 ton and according to the reference plant from report (Tolay, 2011) some important components and the values are given at the Table 3.2.

Table 3.2. The important components of the gasification process and	d the values
---	--------------

Component	Value	Unit
Feed Fuel amount	12.60	Ton/hour
Total energy inlet to reactor	47880000	kcal/hour
%93 pure oxygen to reactor	3.80	Ton/hour
Ash from the reactor	1.10	Ton/hour
Raw syngas amount from reactor	16512	kg/hour
Treated and dry syngas amount	13799	kg/hour
Calorific value of clean sygas	2660	kcal/kg
The energy of final syngas	36701.11	kcal/hour
Gasification efficiency	76.65	%

For energy production conventional solid waste disposal methods are one of the most efficient method. It's known that much more energy gain is available with gasification systems than the conventional systems with the same amount of solid wastes. Moreover, these plants create less waste gases, so air pollution control units are much smaller and more economic than the conventional systems. The form of ash from the gasification systems has inert structure that's why toxic waste management is not necessary.

The feasibilities of plants, which are designed for Çukurkuyu town with two different installed capacities, are shown that they are available to perform. This gasification plant can utilize both municipal solid wastes and agricultural wastes of the town. In this way energy production can be done from these wastes whose transfer effort to landfill site is non-economic. Plus, utilization of these wastes can help to prevent the random solid waste storage and uncontrolled burning of the stubble.

# CONCLUSIONS

Biomass is taken into account to be the important form of energy and having a significant share (10-14 %) in the global energy load, while it has major participant of 90% of total energy supply in the remote and rural areas of the developing world. It is probable to remain the main source of primary energy feedstock for the developing countries in the near future as around 90% of the world population is expected to reside in the developing countries by 2050 (Kucuk & Demirbaş, 1997; Pathak et. al., 2013; Sansaniwala et. al., 2017).

It is supposed that 3 MW installed capacity of the gasification plant is enough to utilize both municipal solid wastes and agricultural wastes at the same time. It also supports the economic development of the town. According to the calculation, expected net profit of the plant is approximately 2.5 M \$ and the investment cost of the gasification plant with 3 MW capacity is around 10 M \$. This means, rate of return time of the plant is almost 4 years. Furthermore, waste heat from the gasification plant is equal to heating energy need of the 1000 households. Çukurkuyu town has less than 1000 households, that's why excess heat can be perfectly utilized for greenhouses of the town. In general view this gasification plant can utilize annually 34.000 tons waste and can produce electricity which is equal to 6500 household need.

This plant creates net zero greenhouse gas emission, especially when it is compared to coal or natural gas electricity production plants. That means, this is an eco-friendly way to manage whole waste from the town.

The construction phase of the planned plant is expected to reach up to 14 month. In this time period wastes can be stored. When we consider the economic income of the town is agricultural and livestock, unused 8550 ha area may be used for growing energy plants which means that the installed plant capacity can be increased up to 6 fold which is equal to 18.8 MW. So that would support the annual income of the town, thus farmers can get extra income. As a result of this, migration to big cities may be prevented and agriculture application may be performed effectively and much more modern. This situation can allow agricultural development.

Especially in the middle Anatolian region, to support the agricultural and livestock applications, to make value added solid wastes, a pilot gasification plant should be constructed to prove this study.

#### ACKNOWLEDGMENT

The authors thank İleri KOÇAK (Mayor of Cukurkuyu Town), Environmental Engineer Merve Behman, Environmental Engineer Cemal Poyraz, Environmental Engineer Orhan Özdemir for their support

#### REFERENCES

- Arnava P., Bruno M. and Coronas J. C. 2010. Review and analysis of biomass gasification models. *Renewable & Sustainable Energy Reviews* **14**(9): 2841-2851.
- Ertürk, F., Akkoyunlu A. & Varinca K. B. 2006. Enerji üretimi Ve Çevresel etkileri. *Stratejik Rapor No: 14, Türkasya Stratejik Araşatırma Merkezi.*
- Klein A., 2002. Gasification: An Alternative Process for Energy Recovry and Disposal of Municipal Solid Waste M.Sc Thesis, *School of Engineering and Applied Science*, *Pennsylvania University*, USA.
- Koç, Y. M. & Garip M. 2008. Türkiye ve Avrupa'da Sürdürülebilir Enerji ve Çevre İlişkisi, VII. Ulusal Temiz Enerji Sempozyumu
- Kucuk, M.M. & Demirbas, A. 1997. Biomass conversion processes, *Energy Conversat Mgmt*, **38**, 151–165.
- Marano M. 2013. The Future of Nuclear Power Domestic and Global, 6th Annual Energy Supply Forum.
- Öztürk K. 2002. Küresel İklim Değişikliği ve Türkiye'ye Olası Etkileri. G.Ü. Gazi Eğitim Fakültesi Dergisi, 22(1), 47-65.
- Seydioğulları H. S. 2013. Renewable Energy for Sustainable Development. *Planlama*, **23**(1), 19-25
- Pathak B., Chaudhari S. & Fulekar M.H. 2013. Biomass resource for sustainable development, *Int J Adv Res Technol*, **2** (6), 271–287.
- Sansaniwala S.K., Pala K., Rosenb M.A. & Tyagia S.K., 2017. Recent advances in the development of biomass gasification technology: A comprehensive review, *Renewable* and Sustainable Energy Reviews, 72, 363-384.
- The World Energy Council, 2016, World-Energy-Resources Report.
- Tolay M. 2011. Katı Atıklardan ve Biyokütleden Enerji Üretimi Teknolojileri ve Entegre Katı Atık Yönetiminde Yatırım Fizibilite Çalışmaları, *Tolay Energy*

## Multicriteria Analysis for Flood Vulnerable Areas in Southeastern Slovakia

# M. Zeleňáková\*1, P. Blišťan2, P. Purcz3 and R. Fijko4

<sup>1</sup>Institute of Environmental Engineering, Technical University of Košice, Slovakia
 <sup>2</sup>Institute of Geodesy, Cartography and Geographical Information Systems, Technical University of Košice, Slovakia
 <sup>3</sup>Institute of Construction Technology and Management, Technical University of Košice, Slovakia
 <sup>4</sup>Institute of Environmental Engineering, Technical University of Košice, Slovakia
 (Corresponding Author's E-mail: martina.zelenakova@tuke.sk)

#### ABSTRACT

Floods are natural phenomena which cannot be prevented. The causes of flooding are extremely heavy rains or rapid melting of snow combined with a significantly reduced ability to detain stormwater in areas. However the negative human-based factors cause changes in runoff ratio and increase the risk of flooding. Human activities change flood behavior in many circumstances. Activities in flood plains and catchment areas such as land clearing for urbanization or agriculture, or construction of infrastructure such as highways, roads and bridges across the flood plain may increase the magnitude of flooding, which in turn increases the damage to property and lives. Determining the flood vulnerable areas is important for decision makers for planning and management activities. Multicriteria analysis methods (MCA) are used to analyze the flood vulnerable areas. Geographical information system (GIS) applications are used for managing, producing, analyzing and combining spatial data. The aim in integrating MCA with GIS is to provide more flexible and more accurate decisions to the decision makers in order to evaluate the effective factors. Some of the causative factors for flooding in watershed are taken into account as daily rainfall, size of watershed, land use, slope and the type of soil. The selection of criteria that has spatial reference is an important step in MCA. The objective of this article is to analyze the flood vulnerability in Bodva river basin, eastern Slovakia. We determined the flood-effective factors, estimate their significance and applied two different approaches of MCA inside the GIS environment.

**Keywords:** Analytical hierarchy process, causative factors, flood risk, geographical information system, ranking method.

#### **INTRODUCTION**

The increase in damage due to natural disasters is directly related to the number of people who live and work in hazardous areas and who continuously accumulate assets. Land-use planning authorities therefore have to manage effectively the establishment and development of settlements in flood-prone areas in order to prevent further increase in vulnerable assets (Petrow *et al.*, 2006) Flood risk analysis provides a rational basis for prioritizing resources and management actions. Risk analysis can take many forms, from informal methods of risk ranking and risk matrices to fully quantified analysis (Hall, 2010).

Multicriteria analysis (MCA) methods have been applied in several studies in flood risk assessment. Yalcin and Akyurek applied a GIS-based multicriteria evaluation in order to analyse the flood vulnerable areas in south-west coast of the Black Sea (Yalcin & Akyurek, 2004). The ranking method and pairwise comparison method were introduced and applied in

this study. Yahaya identified flood vulnerable areas in Hadejia-Jama'are river basin Nigeria by using pairwise comparison method, analytical hierarchy process and ranking method (Yahaya *et al.*, 2010). Kandilioti and Makropoulos applied analytic hierarchy process, weighted linear combination and ordered weighting averaging to precede the overall flood risk map of the area of Athens (Kandilioti & Makropoulos, 2012).

The aim of the presented study is to generate a composite flood vulnerability map of Southeastern Slovakia – Bodva river basin – by mapping the potential natural sources of flooding.

# MATERIAL AND METHODS

## Study area

The river basin Bodva belongs to an international Danube river basin. Slovak part of the river basin Bodva (Figure 1) is defined on the north and east by border with Hornád river basin. From the south the Slovak part of the catchment Bodva is bounded by the border with Hungary and on the west by Slaná river basin.

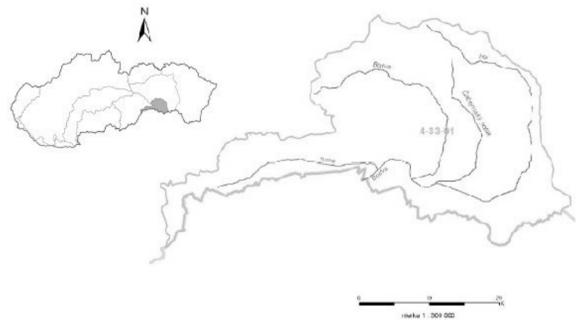


Figure 1. Slovak part of Bodva river basin

Bodva river Basin is situated in the southwestern part of the Kosice region. The river Bodva rises in the mountains Volovske hills, on the northeastern slope of the hill Osadník (1 186 m asl.). Geological structure of the area forms the hydrogeological conditions of the sub-basin Bodva. Basic characteristics of the river basin Bodva contains Table 1.

	-	
	807 827 km <sup>2</sup>	
Area of the Danube river basin		
Area of the Bodva river basin (in the Slovak	$858 \text{ km}^2$	
republic)		
Bordered places of the Bodva basin in Slovakia:		
– the westenest point	Kamenec	48° 33' N 20° 27' E
– the easternest point	Milhosť	48° 33' N 21° 15' E
– the northest point	Kloptaň	48° 47' N 20° 52' E
– the southest point	Kečovo	48° 27' N 20° 28' E
– the highest point	Osadník	1186 m asl.
– the lowest point	Hosťovce	168 m asl.
The total length of the river Bodva in the Slovak	48 km	
republic		
Long-term average flow of Bodva in Host'ovce	$4.48 \text{ m}^3.\text{s}^{-1}$	
The catchment area of Bodva extends into states	Hungary	
Region	Košice	
District	Košice II, Košice –	okolie, Rožňava
Number of villages in the basin area	45	
Population	56 245 (year 2009)	
Land use:	-	
Urban areas	1.6 %	
Agricultural areas	47.1 %	
Forest areas	46.8 %	
Water areas	1.6 %	
Other (industry etc.)	3.4 %	

Table 1. Basic characteristics of the river basin Bodva (2007/60/ES, 2007).

South and east part of Bodva river basin belongs to the district of the climate, which is warm and slightly damp with cold winters. Long-term average annual air temperature is 5 °C to 8 °C. Long-term average rainfall in the basin range from 600 to 1 000 mm.y<sup>-1</sup>. Height and slope conditions affect climatic conditions, especially the size and distribution of rainfall, the air temperature and thus on the overall water balance and runoff regime. There is a predominance of heavy loamy soils and sandy-loam.

# Data

The first step in assessing the flood vulnerability in the study area is to determine the factors affecting the flood on the basis of an analysis of existing studies and knowledge. The criteria used in this study are following: monthly precipitation, basin slope; soil type; land use; and catchment area. The initial data required for this study were acquired from Slovak Hydrometeorological Institute, Digital Terrain Model of the Slovak Republic, Soil Science and Conservation Research Institute, Corine Land Cover, Slovak Water Management Enterprise (Figures 2-6).

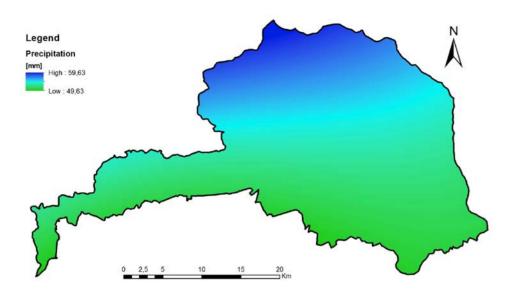


Figure 2. The monthly precipitation.

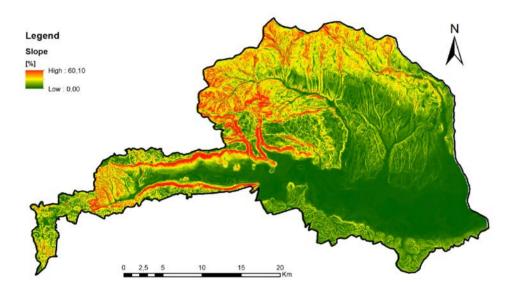


Figure 3. Basin slope.

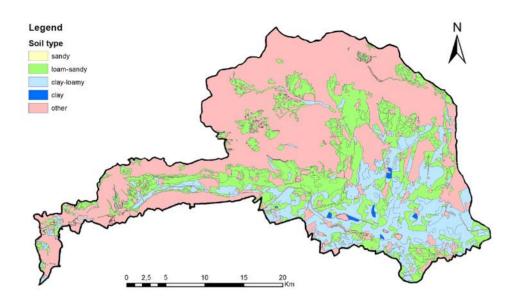


Figure 4. Soil types.

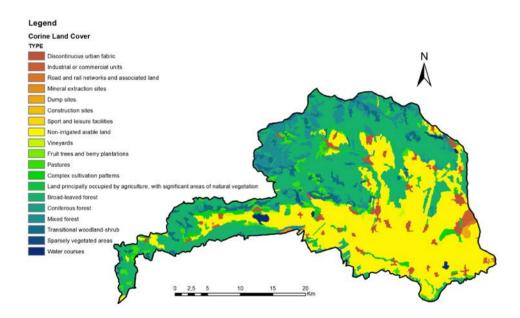


Figure 5. Land use.

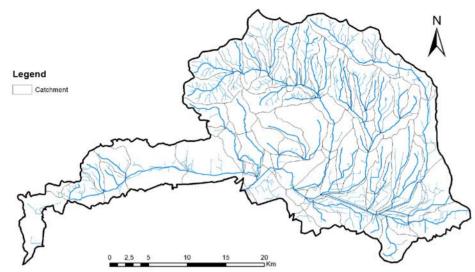


Figure 6. Catchment area.

The Maps of causative factors (Figures 2 - 6) were created in software ArcGIS 10.2 based on background data provided from mentioned institutions.

The criterion values for each factor were divided into five classes according the Table 2 while the inverse ranking (the least important =1, next least important=2 etc.) was applied to these factors.

The next maps, using the division of factors criteria to classes according the Table 2, were also created in ArcGIS 10.2.

			Causative factor	ſS	
Classes	Monthly precipitation (mm)	Basin slope (%)	Soil type (content of clay particles) (%)	Land use (-)	Catchment area (km <sup>2</sup> )
1	0 - 55	0 - 15	0 - 10	forest	0 -10
2	55 - 60	15 - 30	10 - 30	pastures and meadows	10 - 50
3	60 - 65	30 - 45	30 - 45	agricultural land	50 - 100
4	65 - 70	45 - 80	45 - 60	urbanized area	100 - 200
5	70 and more	80 and more	60 and more	water area	200 and more

**Table 2.** The significance of the impact of flooding causative factors.

In this study to analyze flood vulnerability two phases are applied: firstly to identify the effective factors causing floods – the potential natural causes of flooding, and secondly to apply two methods of MCA in GIS environment to evaluate the flood vulnerability of the area.

## Multicriteria analysis methods

We used two methods in determining flood vulnerability – the ranking method and the analytic hierarchy process.

*Ranking method* (RM). RM is used if ordinal information about the decision makers' preferences on the importance of criteria is available. In the first step criteria are ranked in the order of their importance. In a second step, ranking method is used to obtain numerical weights from this rank order (Meyer, 2007). Straight ranking was applied to these factors, which means that 1 is the most important factor and 5 is the least important factor: monthly precipitation = 1; basin slope = 2; soil type = 3; land use = 4; catchment area = 5. The purpose of the criterion weighting is to express the importance of each factor relative to other factors.

Using the ranking method normalized weights of the criterion were calculated as (Eq. 1) (Yahaya *et al.*, 2010):

$$W_j = n - r_j + 1 / \sum (n - r_k + 1) \tag{1}$$

where:

 $W_j$  is the normalized weight for the each factor; *n* is the number of factors under consideration (k = 1, 2...n);  $r_j$  is the rank position of the factor.

Each criterion is weighted (Eq. 2)

$$W = n - r_j + 1 \tag{2}$$

and then normalized by the sum of weights, that is (Eq. 3)

$$\sum (n - r_k + 1) \tag{3}$$

Resulting vulnerability was calculated using the following formula (Eq. 4):

$$IV = \sum (IF_{1j}W_1 + IF_{2j}W_2 + IF_{3j}W_3 + IF_{4j}W_4 + IF_{5j}W_5)$$
(4)

where:

*IV* is index of vulnerability; *IF*<sub>1j</sub>, *IF*<sub>2j</sub>, *IF*<sub>3j</sub>, *IF*<sub>4j</sub>, *IF*<sub>5j</sub> are importance of factor's class;  $W_1$ ,  $W_2$ ,  $W_3$ ,  $W_4$ ,  $W_5$  are the normalized weights for each criterion.

More important factors have greater weighting in the overall evaluation.

Analytical Hierarchy Process (AHP). AHP is a flexible and yet structured methodology for analyzing and solving complex decision problems by structuring them into a hierarchical framework (Saaty, 1980). The AHP procedure is employed for rating/ranking a set of alternatives or for the selection of the best in a set of alternatives. The ranking is done with respect to an overall goal, which is broken down into a set of criteria (objectives, attributes) (Boroushaki & Malczewski, 2008). Twelve river stations in Bodva river basin were assessed.

For each river station a matrix  $5 \ge 5$  – factors  $\ge (1-5)$  was established. This matrix was completed with values from 1 to 5, depending on the class of each factor for the relevant river station in the following way: e.g. when a river station is located in an area where precipitation is class one, the number 1 is written in column "1" for the line "precipitation", and other values on this line are zero. In this way the whole matrix was completed for all factors.

The AHP method programmed in Microsoft Excel was used to determine the weighting of each river station. Matrices were developed for all twelve river stations in Bodva river basins. From the results calculated for separated stations was done interpolation by kriging method (using extension Geostatical analyst) (Blišťan, 2012; Stein, 1999) in ArcGIS 10.2 for the whole area of Bodva river basin.

# **RESULTS AND DISCUSSION**

The multicriteria analysis ends with a more or less stable ranking of the given alternatives and hence a recommendation as to which alternative(s) should be preferred. The spatial variability of flood vulnerability is an important part of flood risk assessment on the national level, as well as for application of spatially differentiated approaches to flood defence strategy (Solín & Skubinčan, 2013).

Regarding our task of flood vulnerability assessment, the result will be a ranking or categorization of areas with regard to their flood vulnerability level, and hence a recommendation as to where flood mitigation action is most required. Weight assessment for causative factors by the ranking method (Table 3) is as follows:

			Causative factor	S	
	Monthly precipitation	Basin slope	Soil type	Land use	Catchment area
Weight	0.333	0.267	0.200	0.134	0.066

Table 3. Weights of causative factors.

A composite map showing the flood vulnerability created using the ranking method with ArcGIS 10.2 is presented in Figure 7.

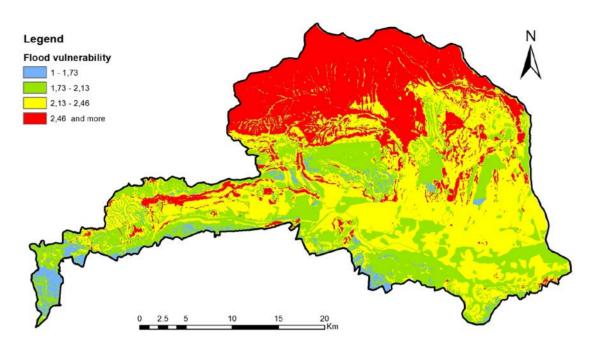


Figure 7. Flood vulnerability of Bodva river basin using the ranking method.

The flood vulnerability in the study area was evaluated in four classes according Table 4. In this application, the flood vulnerability level range as acceptable, moderate, undesirable and unacceptable (Zeleňáková & Gaňová, 2011) on the output map depicting the flood vulnerability in the study area.

 Table 4. Vulnerability acceptability.

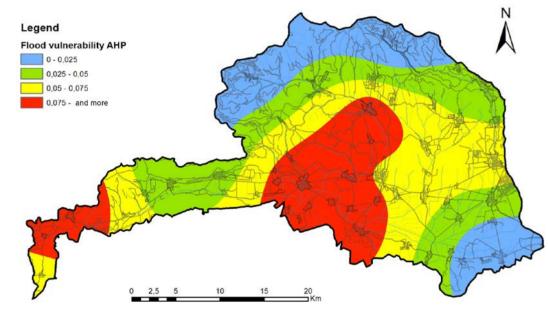
	Vulnarability accortability	Scale of vi	ulnerability
	Vulnerability acceptability	RM	AHP
1	acceptable	1.00 - 1.73	0.000 - 0.025
2	moderate	1.73 - 2.13	0.025 - 0.050
3	undesirable	2.13 - 2.46	0.050 - 0.075
4	unacceptable	2.46 and more	0.075 and more

The resultant weightings with analytic hierarchy process for all river stations are shown in Table 5.

**Table 5.** Weights of river stations.

River station	Weight
Štos	0.051097
Zlata Idka	0.051097
Perín	0.051097
Jablonov nad Turňou	0.071072
Malá Ida	0.080109
Košice - Šaca	0.090646
Kečovo	0.087918
Moldava nad Bodvou	0.090646
Jasov	0.103193
Janík	0.103598
Turňa nad Bodvou	0.108868
Silica	0.110658

River stations are ranked by the value of weightings from largest to smallest.



The obtained results from software ArcGIS 10.2 are presented in Figure 8.

Figure 8. Flood vulnerability of Bodva river basin using analytic hierarchy process.

The flood vulnerability assessment based on the analytic hierarchy process shows that the Bodva river basin is mainly in areas with moderate and undesirable flood vulnerability. Zones with unacceptable and acceptable level of flood vulnerability were also identified, in smaller areas. The similar results – presence mainly of moderate and undesirable flood vulnerability are shown also by ranking method in the study area – although space assessment of acceptable and unacceptable flood vulnerable areas by both methods are prove completely different results. Preliminary flood risk assessment which has been done in the Slovak Republic based on requirements of European Union – 2007/60/EC (Flood directive) in 2011 prove that results

obtained by ranking method are more precisions than that obtained by analytic hierarchy process.

# CONCLUSION

Flood vulnerability is a common effect of two independent mechanisms natural conditions and the human activities in the basin. The primary impulses of floods are usually extremely intense precipitation. The total catchment's hydrological response to intense rainfall is determined by its natural environment, a whole complex of characteristics of the basin (Zeleňáková, 2009). Some of them may be a process initiated by the intense rain accelerate, respectively amplified.

The aim of the present study was to generate a composite map for decision makers using selected factors causing floods. In the analyses, some of the causative factors for flooding in a basin area are taken into account, such as soil type, precipitation, land use, size of the catchment and basin slope. A case study of flood vulnerability identification in the Bodva catchments' areas in eastern Slovakia is employed to illustrate the different approaches. A geographical information system (GIS) is integrated with multicriteria analysis (MCA) in the paper. We created two multicriteria vulnerability maps for Bodva river basin. Our pilot study showed significant differences between both methods shown in Figure 7 and 8. The different results obtained from these two methods indicate the importance of the decision maker in determining the weights and the proper method, and making the decision. The weighting of the criteria significantly affects the results of the overall evaluation.

We can say, that the results obtained by the ranking method are more representative. The same results were proved by other studies (Yalcin & Akyurek, 2004; Yahaya *et al.*, 2010) regarding the same topic. In the case of flood vulnerability assessment for Bodva river basin AHP method is not suitable. It should be noted that RM method shows the best results comparing the existing flood in the recent years. The development of RM method for whole catchment has the advantage that there is a method which is easy to apply.

## ACKNOWLEDGMENT

The contribution is written thanks to support of project VEGA 1/0609/14.

## REFERENCES

- Blišťan P. 2012. Interpolation methods for modeling and visualization of spatial phenomena in GIS environment. *Fyzikálne faktory prostredia* 2, 99 105.
- Boroushaki S. & Malczewski J. 2008. Implementing an extension of the analytical hierarchy process using ordered weighted averaging operators with fuzzy quantifiers in ArcGIS. *Computers & Geosciences* 34, 399 410.
- Hall J. 2010. Editorial: Journal of Flood Risk Management. J Flood Risk Manage, 3, 1–2.

Implementation of directive 2007/60/ES of 23rd October 2007 on flood risk assessment and management: Preliminary flood risk assessment in Bodrog river basin, Attachments. MoE (Ministry of Environment), SWME (Slovak Water Management Enterprise). [online]. Available at: http://www.minzp.sk/files/sekcia-vod/bodrog-prilohy.pdf

Kandilioti G. & Makropoulos Ch. 2012. Preliminary flood risk assessment. The case of

Athens. Natural Hazards 61, 441 - 468.

- Meyer V., Scheuer S. & Haase D. 2009. A multicriteria approach for flood risk mapping exemplified at the Mulde river, Germany. *Natural Hazards* 48, 17 39.
- Petrow T., Thieken A.H., Kreibich H., Bahlburg C.H. & Mercz B. 2006. Improvements on Flood Alleviaton in Germany: Lessons Learned from the Elbe Flood in August 2002, *Environmental Management* 38, 717 732.
- Saaty T.L. 1980. *The Analytic Hierarchy Process*: Planning, Priority Setting, Resource Allocation, McGraw-Hill International Book Co., New York, NY, p. 437.
- Solín Ľ. & Skubinčan P. 2013. Flood risk assessment and management: review of concepts, definitions and methods. *Geographical Journal* 65, 23 44.
- Stein M.L. 1999. Interpolation of Spatial Data. Springer-Verlag New York, p. 247.
- Yahaya S., Ahmad N. & Abdalla R.F. 2010. Multicriteria Analysis for Flood Vulnerable Areas in Hadejia-Jama'are River Basin, Nigeria. European Journal of Scientific Research 42, 71 - 83.
- Yalcin G. & Akyurek Z. 2004 Analysing flood vulnerable areas with multicriteria evaluation. In *Proceedings from XXth ISPRS Congress of Geo-Imagery Bridging Continents*, pp. 359–364.
- Zeleňáková M. 2009. Preliminary flood risk assessment in the Hornád watershed. In: *River Basin Management 5*, Southampton: Wessex Institute of Technology, 15 24.
- Zeleňáková M. & Gaňová L. 2011. Integrating multicriteria analysis with geographical information system for evaluation flood vulnerable areas. In: *Proceedings of the 11th International Multidisciplinary Scientific GeoConference, SGEM 2011*. Bulgaria, Sofia: STEF92 Technology, 433 - 440.

# Comperatively Investigation Pretreatments of H<sub>2</sub>SO<sub>4</sub> and Ultrasound Effect for Corncob to Increase Available Bioenergy Potential by Response Surface Methodology

# E.Ü.Deveci and Ç. Gönen\*

<sup>1</sup>Department of Environmental Engineering, Nigde Ömer Halisdemir University, Nigde, Turkey. (Corresponding Author's E-mail: cagdas.gonen@gmail.com)

## ABSTRACT

Bioenergy is a sort of renewable energy source, such as bioenergy, bioethanol, biogas or bioethanol, and it has widespread application in the world. The main purpose of this work is to optimize the physicochemical processes of sulfuric acid and ultrasound + sulfuric acid pretreatment application to get more energy per unit mass from the corncob. In order to optimize the best reaction conditions, a statistical experimental design method which is Box Behnken was used. The parameters such as acid concentration, temperature, reaction time, ultrasound power were selected as the factors to be optimized. The solid concentration was fixed at 1% and the particle mesh size was fixed at 0.2. In acid pretreatment, the highest total sugar concentration according to the statistical software model is 5.05 g/L in 4.74% acid concentration, 100 °C temperature and 117 min reaction time. If the concentration of reducing sugar is desired to be maximum in the acid pretreatment, a concentration of 5% acid, 80°C temperature and a reaction time of 180 minutes can be obtained. In ultrasound supported acid pretreatment application, while total sugar concentration rise up to 22%, reduced sugar concentration increased up to 70%. Finally it could be said that ultrasound assisted acid pretreatment has much more effective than the solely acid pretreatment.

Keywords: Corncob, renewable energy, RSM.

## **INTRODUCTION**

It's expected that, in a sort time, fossil fuels have been shifted intensively to renewable sources. The unsolvable disadvantages of the fossil fuels such as energy crises, global environmental problems, fluctuation of the oil price and energy security issues enforced the countries to choose and investigate renewable energy sources which have to be appropriate the countries natural sources. Especially alternative renewable sources like biomass and biofuels from biomass have been attractive day by day (EBA, 2017).

Biomass have organic content, biological basis, unlike fossil fuels, which main composition is carbon compounds. Additionally, biomass is well known renewable source. Liquid and gas phase biofuels to produce electricity, thermal power and other some kind of chemicals as by product have been produced from biomass and other organic wastes. That's why developed and under developed countries prefer the biomass sources in a large scale (Koçar et. al., 2013).

It is suppose that the 805 of energy consumption is dependent on the fossil fuels. This

situation has caused not only the climate change but also devastate the natural energy sources. Therefore almost all countries interested in clear, ecofriendly and renewable energy sources. According to international energy agency (IEA) 14% of the worlds' total energy need was met with the biomass energy in 1998 (Adigüzel, 2013).

Turkey was taken a decision about biofuel production by Turkey Energy Market Regulatory Authority (EMRA) at 29.07.2011 with a regulation. According to regulation, biofuel, which produced from domestic agricultural products, must be added to fuels at least 2% after 1 January 2013 and must be added at least 3% to fuels after 1 January 2013. This produced biofuels has no tax (private consumption tax - OTV) obligation.

It was suggested that if the mixing ratio of the produced bioethanol to gasoline is 3% in Turkey, the cost of petroleum import can decrease to 385 billion dollars. If the mixing ratio of produced bioethanol to gasoline is also 5%, the expenditure for petroleum import can decrease to 596 billion dollars (Polat et. al. 2009). If small or medium scale biofuel facility will set up around Niğde region, this can be contributed to economy of country. According to the data of energy ministry, Turkey consumed three times higher energy than the produced energy and 70 % of consumed energy was imported. Therefore, renewable energy sources such as biomass could be used for producing electric and thermal energy and it is attractive option.

In energy market, using of renewable raw material have been get more and more important day by day. Because of more popularity of the sustainability concept, main target is zero  $CO_2$  emission for electricity production, travelling and heating. To access of main target, even if other renewable energy sources such as the sun and wind are popular today, it is problem that waiting for solution because of fluctuating according to the hours of the day and electricity production is not to be constant. For renewable energy, agricultural biomass and also animal waste is the most reliable. For example, The United States National Research Council aims to convert 10% of liquid fuels and 50% of organic chemicals into renewable biomass in 2020.

Turkey's renewable energy consuming ratio in energy consumption is 13% between 2000 and 2013, these ratios fluctuated about 9-10% between 2004 and 2013. As share of biomass energy in energy production was 14 % in 1990, these share dropped back 3% in 2012, because total energy consumption was increased enormously (Akçiçek, 2015).

Biomass includes various kind of source such as agricultural waste, wood industry wastes, animal livestock waste or agro-industrial wastes. Biomass cannot utilize directly microorganisms and it has extremely low degradability, due to the heterogeneity and crystallinity properties of the lignocellulosic structure in biomass (Datara et. al. 2007). Consequently there is a need to improve pre-treatment process on lignocellulosic structure to convert it into a usable structure for microorganisms. In this study, due to increase production efficiency in biofuel production and be able to use microbial conversion technique, experiments were carried out chemical pretreatment ( $H_2SO_4$ ). Corncob is valuable agricultural waste, whose content is including 30-35 % hemicellulose, 40-45 % cellulose and 10-20 % lignin. Converting this agricultural waste, which has a very low economic value, to a value-added product such as biofuels is more important as a renewable resource (Sheng & Marquis, 2006). However, due to its lignin content, it is

very difficult to be converted into fermentable sugar. Thus it must be applied either chemical or biological pretreatment (Mosiera et. al., 2005).

Experimental design methods using in experimental studies is very effective method to find factors and their effect way and also to make the optimization of parameters. The Box–Behnken experimental method is a three-level fractional factorial design and it used to determine the effect of factors in the experimental zone. This design is a combination of a two-level factorial design with an incomplete block design. In this study, it was used Box-Behnken experimental design for optimization pretreatment. In this study, acid pretreatment was applied corn cob by Box-Behnken.

# MATERIALS AND METHODS

The raw material of Corncob was collected from local market and air dried. After chipping and rendering, corncob was sieved by a 0.2 mesh screen and stored for future use at + 4 °C.

Box-Behnken experimental method used to optimize the factors which are time, temperature and acid ratio for the response of total sugar concentration and reduced sugar concentration. The independent variables, levels and their values are shown in Table 1. and 5. center point added to experimental design in without Ultrasound experiments. Table 2. Indicate the experimental design setup for ultrasound experiments. All experiments were made with 2 replicate and all analyses was made in 3 replicated. The ranges of factors were selected based on previous experimenes.

STD order	Acid %	Temperature °C	Time (min)	Acid %	Temperature °C	Time (min)
1	-1	-1	0	1	50	105
2	+1	-1	0	5	50	105
3	-1	+1	0	1	100	105
4	+1	+1	0	5	100	105
5	-1	0	-1	1	75	30
6	+1	0	-1	5	75	30
7	-1	0	+1	1	75	180
8	+1	0	+1	5	75	180
9	0	-1	-1	3	50	30
10	0	+1	-1	3	100	30
11	0	-1	+1	3	50	180
12	0	+1	+1	3	100	180
13	0	0	0	3	75	105
14	0	0	0	3	75	105
15	0	0	0	3	75	105
16	0	0	0	3	75	105
17	0	0	0	3	75	105

Table 1. Independent variables of design, coded view and values of factors without US

In experiments working volume of the experiment was 250 ml in glass bottle. Initial solid concentration is 1%. Ultrasound experiments made with temperature controlled shaker at 200 rpm. Ultrasounds experiments made with Hielscher UP400S. All samples firstly

filtered through filter paper and then centrifuged with 10.000 rpm at 10 minute, finally supernatant used for the total sugar and reduced sugar analyzed. For total sugar amount was calculated according to approach of Dubois, 1956 (Dubois et. al., 1956) and reduces sugar concentration was determinated using with Dinitrosalisilik acid (DNS) method (Miller, 1959). Design expert software (trial version) was used for experimental design.

STD order	US Kj/kgDM	Acid %	Time (min)	US Kj/kgDM	Acid %	Time (min)
1	-1	-1	0	100	1	17,5
2	+1	-1	0	60	3	17,5
3	-1	+1	0	60	3	17,5
4	+1	+1	0	100	5	17,5
5	-1	0	-1	60	3	17,5
6	+1	0	-1	100	3	5
7	-1	0	+1	20	3	30
8	+1	0	+1	60	3	17,5
9	0	-1	-1	20	3	5
10	0	+1	-1	20	5	17,5
11	0	-1	+1	20	1	17,5
12	0	+1	+1	60	5	30
13	0	0	0	60	3	17,5
14	0	0	0	60	1	30
15	0	0	0	60	1	5
16	0	0	0	60	5	5
17	0	0	0	100	3	30

Table 2. Independent variables of design, coded view and values of factors with US

# **RESULT and DISCUSSION**

Box-Behnken experimental design method was used to optimize the factors of acid ratio, temperature and time to find maximize for total sugar concentrations from the corn cob. Initial solid concentration of corn cob is 1% (w/v). High level, low level of the factors and the response of the total sugar concentrations was shown at the Table 3.

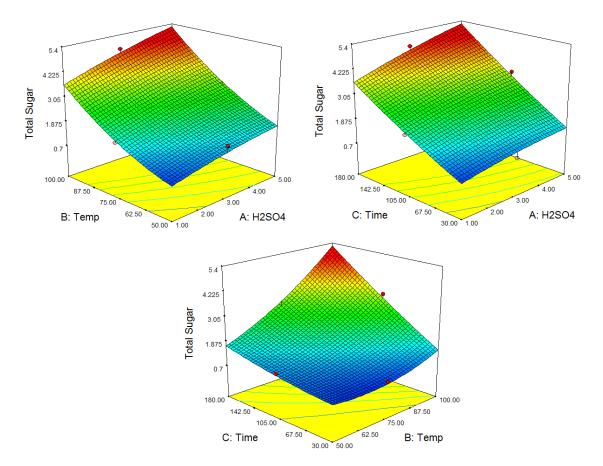
# Acid Pretreatment

From the software, Box Behnken model is significant according to ANNOVA test and value of the model is 0.95. Maximum conversation ratio is about 47% according to experimental model.

As Figure 1a it is clear that the maximum total sugar concentration is 4.71 g/L when the temperature is 100 °C and  $H_2SO_4$  ratio is 5%. As shown in Figure while both temperature and acid ratio decrease total sugar concentration decline to 0.48 g/L from 4.71 g/L. According the Figure 1a, the effect of temperature is more significant than the acid ratio change. Figure 1b show the effect of both time and acid ratio. As Figure 1a maximum total sugar concentration is 4.71 g/L when the time is 180 min and acid ratio in high level. The factor of time has clearly significant effect on the total sugar production. Interaction effect of both time and temperature effect is clearly high as Figure 1c. The graph shows that

exponential increase of total sugar concentration up to 4.71 g/L

Brodeur *et.al* (2011) reported that if the lignocellulosic content is lower than the corn cab it's probably the low level of temperature is enough to degradation. Produced total sugar amount is linked with the lignocellulosic content. From Barışık et.al. (2016) the effect acid is enlarge when the temperature get higher. According to report from Barışık et.al. (2016) pretreatment was applied to straw samples with Box-Behnken method. The optimum process conditions for maleic acid were, 210°C, 1.08% acid concentration and 19.8 min; for succinic acid 210 °C, 5% acid concentration and 30 min; for oxalic acid 210 °C, 3.6% acid concentration and 16.3 min. The ethanol concentrations obtained at optimum conditions were 12.9, 10.3 and 12.9 g/L for maleic, succinic and oxalic acid pretreatments, respectively. These results indicate that, organic acids decomposition of lignocellulosic structure is effectively. On the other hand, maleic and oxalic acids show to be more effective compared to succinic acid. In this study which it was H<sub>2</sub>SO<sub>4</sub> pretreatment and corn cob as substrate, optimum temperature 100°C was determined which was the highest temperature of experimental value. According design, model is significant and R<sup>2</sup> value is 0.88 for reduced sugar production. Reduced sugar concentration can reach up to maximum 2.1 g/L. The independent variables values of the maximum reduced sugar concentration is similar with the conditions of maximum total sugar concentration, which are 5% acid ratio, 180 minute and 100 °C.



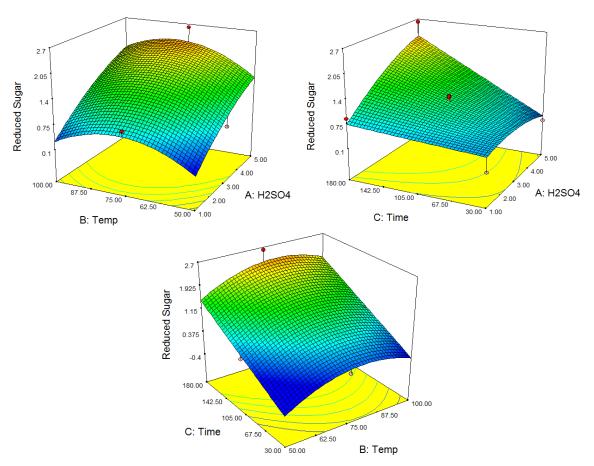
**Figure 1.** Response graphichs of total sugar (g/L) for box behinkein experimental design a) temperature ( $^{\circ}$ C) and acid ratio (%), b) time (min) and acid ratio (%) c) time (min) and temperature ( $^{\circ}$ C) interactions.

In order to effective pretreatment for acid pretreatment, it requires high temperature and pressure and also dilute acid pretreatment is the most effective process for lignocelluloses. End of this process, lower degradation products is generated than concentrated acid pretreatments (Kumar et. al., 2009). The report from Saha et. al was indicate that the effects of temperature (140, 160 and 180 °C) on dilute H<sub>2</sub>SO<sub>4</sub> (0.00, 0.25 and 0.50%, v/v) pretreatment of wheat straw for 15 min and subsequent enzymatic saccharification (45 °C, pH 5.0, 72 h) were evaluated. Dilute acid (0.5%, v/v) pretreatment at 180 °C for 15 min and after enzymatic saccharification using the commercial cellulase and a  $\beta$ -glucosidase preparation produce 576 mg total sugars per gram dry solid of wheat straw (75% yield) (Saha et. al., 2005).

From the graphichs acid ratio is significantly effected the reduced sugar concentration as Figure 2a. Chemical pretreatment has become one of the most promising methods to improve the biodegradability of cellulose by removing lignin and/or hemicelluloses, and to decrease the degreeof polymerization (DP) and crystallinity of the cellulosic component in lignocelluloses (Mtui, 2009; Agbor et. al., 2011) generally dilute acids concentration are ranging from 0.1% to 2%(w/v) in the acid pretreatment methods. Gütsch et. al. (2012) were studied three different acids (acetic (0.02–0.15 M), oxalic (0.01–0.1 M) and sulfuric acid (0.01–0.1 M)) for their catalytic activity during the pretreatment of Eucalyptus globulus wood. In this sdudy, the reactor was heated up to prehydrolysis temperature (120-200 °C) within minimum heating time (approximately 30 min), the temperature was maintained for the prehydrolysis time (10-120 min). Result of this study, convertion ratio was up to 95 % in experiment condition for Eucalyptus globulus wood. Yu et al. (2012) indicate that a total xylose recovery of 79.6% for sweet sorghum bagasse in a step-change flow rate reactor (184 °C, 20 ml/min, 8 min, and 10 ml/min, 10 min) and a total xylose recovery of 84.4% for eucalyptus wood chips in the batch stirred reactor (184 °C, 5% w/v, 18 min). Another study from Wang et al. (2009) reported up to 40% of cellulose conversion, when spruce wood chips were used for pretreatment at 180 °C with an acid concentration of 1.84% followed by disk milling. Though, acid methods is less attractive due to the formation of inhibitory compounds, equipment corrosion, toxicnature, and high operational and maintenance costs. In this study, conversion ratio was determined as 47% for total sugar and % 21 for reduced sugar which maximize condition was 5 % H<sub>2</sub>SO<sub>4</sub> and 100 °C in 180 min.

From the Figure 2b, acid ratio is not significantly effect the reduced sugar concentration solely, but on the other hand when acid ratio was analysed with the factor of temperature and timereduced sugar production was obviously changed in positive way. From the Figure 2c, interaction with time and temperature factors are clearly important to reduces sugar concentration. Highest reduced sugar amount of about 2.0 g/L was observed at the mid point of temperature which is 75 °C and at 180 min reaction time. Numerical optimization of model for reduced sugar production indicate that to maximize the reduced sugar production, which is 2.218 g/L, the factors of temperature, acid ratio and time value have to be 75 °C, 5% and 180 min respectively.

Eurasian Journal of Environmental Reseach 1 (1) www.cessciencegroup.com



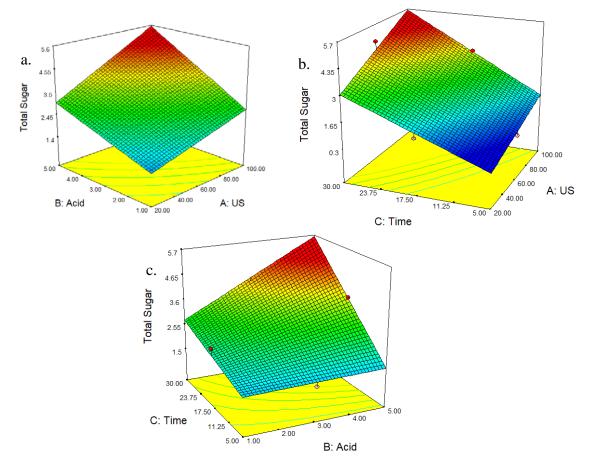
**Figure 2**. Response graphichs of reduced sugar (g/L) for box behinkein experimental design a) temperature (°C) and acid ratio (%), b) time (min) and acid ratio (%) c) time (min) and temperature (°C) interactions.

# **US+Acid Pretreatment**

The second series of pretreatment processes were carried out with ultrasound and acid. The results of optimization study of pretreatment studies with ultrasound and sulfuric acid are explained in the following graphs. The change in both total sugar and reducing sugar concentration values has been studied.

The Figure 3a shows the total sugar concentration depending on the acid concentration of and ultrasound power change. A growing in total sugar concentration for increased ultrasound power and an increase in total sugar concentration for ascending acid concentrations were observed. A much larger rise in sugar concentration is seen when the common effect of both factors is considered. The highest total sugar concentration was 5.6 g/L. This value is obtained at the point where the acid concentration and ultrasound power are maximum. Figure 3b is a graph showing the effect of time factors and ultrasound power factors. From the graph, similar to the previous graph, the increase in ultrasound power also resulted in an rise in total sugar concentration. When the time factor is examined, the total sugar concentration obtained with the elongation of the reaction time is also increased. when the effect of both factors was examined, the total sugar concentration reached to much higher levels and it had a value of 5.7 g/L. The graph of acid concentration and reaction time is shown in Figure 3c. It is clearly

shown in the graph that the acid concentration and the reaction time together have an effect on the total sugar concentration on the positive side. Factors, when examined alone, are not as high as the effects they have created, although there is an increase in total sugar concentration

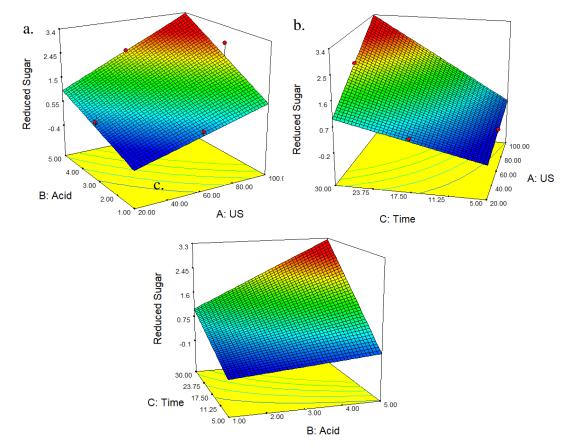


**Figure 3.** TS concentration optimization (g/L) for Box Behnken experimental design a) US power and acid ratio (%), b) time (min) and US power c) time (min) and acid ratio (%), interactions.

In our study total sugar concentration rise up to 22% with support of US application like the other studies explained below; In the study conducted by Ebringerová and Hromádková, the effect of ultrasound on the hemicellulosic extraction of the corn cob was studied. In this study, in the first stage direct extraction in the H2O2-alkali treatment, in the second stage H2O2-alkali with ultrasound was applied. According to the results obtained, it was determined that the total carbohydrate content increased by 10-40% in all ultrasound results compared to the results of the treatment where only H2O2-alkali treatment was performed (Ebringerová and Hromádková, 2002). Jacquemin et al. (2012) carried out that it was aimed to develop an environmentally friendly process by combining the hemicelluloses of wheat straw and dandruff into fractionated and technical aspects (yield, purity) combined with environmental characterizations (water consumption, carbon dioxide emissions). Plus, ultrasound effect was investigated in the study. According to the obtained results, the content of arabionase sugar increased by 34.1% with ultrasound applications. Hromádková et al (1999). determined that xylan extraction from corn cobs increased to 21.9% and 36.8% xylan contents when alkali extraction was supported by

ultrasound application. Zhang et. al. (2008) compared the differences of raw material structure and subsequent saccharification rate before and after ultrasonic pretreatment of lignocellulosic biomass. They pointed out that the ultrasonic vibration energy is too low to change the surface conformation of the raw material particle. Ultrasound pretreatment, the lignin degradation and enzymatic saccharification rates are effectively improved.

Diagrams of the changes in reducing sugar concentrations in the optimization studies are given in Figure 4. Optimized factors in these experiments are the acid concentration, ultrasound power and reaction time. From the Figure 4a, an increase in the concentration of reducing sugar with an increase in acid Concentration and ultrasound strength was observed, which increased to 3.4 g / L. Similarly, Figure 4b indicate that the duration of the reaction and ultrasound power change. It is seen that the concentration of reducing sugar at the maximum levels of the factors also reaches the maximum level. Reduced sugar concentrations obtained due to changes in reaction time and acid concentration are shown in Figure 4c. The longest reaction time was 30 minutes and the maximum acid concentration was 5%, which cause the highest level of reducing sugar, up to 3.3 g/L.



**Figure 4** RS concentration optimization (g/L) for Box Behnken experimental design a) US power and acid ratio (%), b) time (min) and US power c) time (min) and acid ratio (%), interactions.

# CONCLUSION

Chemical pretreatment is used for lignocellulosic material which is agricultural waste, agroindustrial waste such as sugar beet,corn cob and sugar cane, forestry residues. The chosen pretreatment is so important because of different properties waste. Moreover, some studies have been reported chemical, biological and advanced application such as AFEX pretreatment, which become interesting for industrial applications.

In this work, H2SO4 acid hydrolysis pretreatment was applied to decompose the lignocellulosic and cellulosic structure of corncob in order to maximise the sugar conversion by RSM method of Box Behnkein. Different factors of temperature, acid concentration and reaction time was applied to optimization of factors to maximize sugar and reduced sugar concentration. According the model solutions, the maximum total sugar concentration of 5.05 g/L can be obtained at the conditions of 4.74% acid concentration, 99.55 °C and 177 min. and also the reduced sugar concentration can be reach up to 2.20 g/L.

According to results from this study it clear that the ultrasound power can increase the total sugar and reduced sugar concentration, 22% and 70% respectively, from the corncob to improve the bioavailability of the biomass to produce more efficient biofuel production for per mass unit raw material of corncob.

# ACKNOWLEDGMENT

The authors thank Omer Halisdemir University, Scientific Research Project Funding (OHU-BAP) for their financial support [Project number: BAP FEB2015-42-BAGEP].

# REFERENCES

- Adıgüzel A.O. 2013. Biyoetanolün Genel Özellikleri ve Üretimi İçin Gerekli Hammadde Kaynakları, *BEÜ Fen Bilimleri Dergisi*, **2**, (2), 204-20.
- Agbor V.B., Cicek N., Sparling R., Berlin A. & Levin D.B. 2011. Biomass pretreatment: fundamentals toward application, *Biotechnol. Adv.*, **29**,675–85.
- Akçiçek Ö. 2015. Ekonomik Büyüme ve Yenilenebilir Enerji Tüketimi Üretimi İlişkisi; Türkiye Örneği, Yüksek Lisans Tezi, Anadolu Üniversitesi Eskişehir.
- Barisik G., Isci A., Kutlu N., Bagder Elmaci S. & Akay B. 2016. Optimization of organic acid pretreatment of wheat straw, *Biotechnology Progress*, **32** (6) 1487-1493.
- Brodeur G., Yau E., Badal K., Collier J., Ramachandran K. B. & Ramakrishnan S. 2011. Chemical and Physicochemical Pretreatment of Lignocellulosic Biomass: A Review, *Enzyme Research*, Volume 2011, Article ID 787532, 17 pages.
- Datara R., Huanga J., Manessa P., Mohagheghia A., Czernika S. & Chornetb E. 2007. Hydrogen production from the fermentation of corn stover biomass pretreated with a steam-explosion process, *International Journal of Hydrogen Energy*, **32**, 8, 932– 939.
- Dubois M., Giles K.A. & Hamilton J.K. 1956. Colorimetric method for determination of sugars and related substances. *Analytical Chemistry*, **28**, 350-356.

- EBA, EBA Biomethane & Biogas Report 2015, http://europeanbiogas.eu/2015/12/16/biogasreport2015/, (accessed February 2017)
- Ebringerová, A, Hromádková Z. 2002. Effect of ultrasound on the extractibility of corn bran hemicelluloses, *Ultrasonics Sonochemistry*, **9**, 4, 225-229
- Gütsch J.S., Nousiainen T. & Sixta H. 2012. Comparative evaluation of autohydrolysis and acid-catalyzed hydrolysis of Eucalyptus globulus wood, *Bioresource Technology* **109**, 77–85
- Hromádková Z, Kováciková J, Ebringerová A. 1999. Study of the classical and ultrasoundassisted extraction of the corn cob xylan. *Industrial Crops and Products*, **9**(2),101–9
- Jacquemina, L., Zeitouna, R., Sablayrolles C., Pontalier P., Rigal L. 2012. Evaluation of the technical and environmental performances of extraction and purification processes of arabinoxylans from wheat straw and bran, *Process Biochemistry*, 47, 373–380
- Koçar G., Eryaşar A., Ersöz Ö. & Arıcı Ş. 2013. Biyokütle Enerjisine Sektörel Yaklaşım: İzmir Örneği, *Mühendis ve Makina*, **54**, (689), 78-85.
- Kumar P., Barrett D. M., Delwiche J. & Stroeve P. 2009. Methods for Pretreatment of Lignocellulosic Biomass for Efficient Hydrolysis and Biofuel Production, *Ind. Eng. Chem. Res.*, 48 (8), 3713–3729
- Miller, G.L. 1959. Use of dinitrosalicylic acid reagent for determination of reducing sugar. *Analytical Chemistry*, **31**, 3, 426-428.
- Mosiera N., Wymanb C., Dalec B., Elanderd R., Leee Y.Y., Holtzapplef M. & Ladischa M. 2005. Features of promising technologies for pretreatment of lignocellulosic biomass, *Bioresource Technology*, 96, 6, 673–686.
- Mtui Y.S. 2009. Recent advances in pretreatment of lignocellulosic wastes and production of value added products, *Afr J. Biotechnol.*, **8**, 1398–1415.
- Polat F. & Aksu T. 2009. Yenilenebilir Enerji Kaynağından Potansiyel Yem Kaynağına Giden Yol: Damıtık Tahıllar I- Damıtık Tahılların Elde Edilişi ve Nitelikleri, *Atatürk Üniversitesi Vet Bil Derg*, **4**, (3).
- Saha B.C., Iten L.B., Cotta M.A. & Wu Y.V. 2005. Dilute acid pretreatment, enzymatic saccharification and fermentation of wheat straw to ethanol, *Process Biochemistry*, 40:12, 3693–3700.
- Sheng J., Marquis R.E. 2006. Enhanced acid resistance of oral streptococci at lethal pH values associated with acid-tolerant catabolism and with ATP synthase activity. *FEMS Microbiol. Lett.*, **262**, 1, 93–98.
- Wang Gleisner R. 2009. Sulfite pretreatment (SPORL) for robust enzymatic saccharification of spruce and red pine, *Bioresource Technology*, **100**,8, 2411–2418
- Yu Q., Zhuang X., Wang Q., Qi W., Tan X., Yuan Z. J.Y., Zhua X.J. & Pan G.S. 2012. Hydrolysis of sweet sorghum bagasse and eucalyptus wood chips with liquid hot water, *Bioresour Technol*, **116**, 220-5
- Zhang Y., Fu E., Liang J. 2008. Effect of ultrasonic waves on the saccharification processes of lignocellulose, *Chem. Eng. Technol.*, **31**, 1510-1515