Engineering Approaches on Sustainability

In general terms, sustainability is the act of meeting our own needs today without compromising the ability of future generations to meet their own needs (World Commission on Environment and Development, 1987). Obviously, the ability of natural resources and environmental systems to support our needs is limited. Therefore, the major challenge for engineers today is to design and/or operate systems that use energy and natural resources sustainably. Designing for the environment is crucial. This book presents the recent engineering approaches to sustainability from research and practice.

The chapters included in this volume are from the first International Sustainability Congress organized by International Center of Sustainability (ICS) between 1-3 December 2016 in Istanbul, Turkey. All chapters are peer-reviewed by both the editors and at least two independent scholars from fields relevant to the manuscript's subject area. ICS is a research and academic center for sustainability founded in 2015 and dedicated to build resilience of communities and ecosystems to environmental and socio-economic risks. ICS has an integrated approach and defines sustainability not only in terms of environment but also in terms of socio-economic process. Its mission is to produce information, to research and to practice at Micro and Macro levels in Sustainable Development with a holistic and cross-disciplinary approach.

IJOPEC PUBLICATION
London Istanbul

ISBN 978-0-9932118-2-9

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ENGINEERING APPROACHES ON SUSTAINABILITY

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International Journal of Politics & Economics
London, United Kingdom
3 Bassingbourn, HouseSutton Dwellings
Upper Street, London N1 1UB

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E-Mail: info@ijopoc.co.uk
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Engineering Approaches on Sustainability
First Edition, December 2016
IJOPEC Publication No: 32

ISBN: 978-0-9932118-2-9

A catalogue record for this book is available from Nielsen Book Data, British Library and Google Books.

The cover illustration is designed by Res. Assist. Neslihan Alpay, Marmara University, Metallurgical and Materials Engineering Department

Printed in Turkey.
Kayhan Printing Co Ltd.
Merkez Efendi Mh. Fazıl Paşa Cd. No: 8/2
Zeytinburnu / İstanbul, Turkey
Phone: (+90) 212 576 0136

Composer:
IJOPEC Art Design
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Introduction Engineering Approaches on Sustainability

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Sustainability undoubtedly is among the most critical challenges that our modern world faces today. Being aware of this fact, Marmara University International Center of Sustainability (ICS) organized an international congress between 1-3 December 2016 in İstanbul, Turkey, in order to facilitate expert discussions about recent innovations in sustainability. The main themes of the discussions were environmental, economic and social sustainability with a focus on recent innovations in these areas.

This book is prepared to present you with the selected topics of engineering approaches addressed during the congress. Each chapter in the book is dedicated to one selected engineering article. All chapters are peer-reviewed by both the editors and at least two independent scholars from fields relevant to the manuscript's subject area.

The issues discussed in each chapter deals with a different aspect of environmental sustainability. Here in this book you will find topics mainly related to

I. renewable community power which allows communities to develop, deliver and benefit from sustainable energy,

II. other sustainable energy aspects such as; gaining energy from waste, more efficient energy consumption, energy efficient buildings, and eco-friendly, energy efficient refrigeration systems,

III. sustainable environmental engineering practices such as; using waste to treat wastewater, separation of valuable materials from wastewater, innovative water and wastewater treatment techniques,

IV. sustainable production of raw materials from waste to reduce and manage solid waste

V. environmentally sustainable management systems such as; innovative domestic wastewater management via segregated streams, rainwater harvesting, and more specific management systems such as airport deicer management, and fisheries management.

We would like to express our sincere thanks to all our contributors for their support. Without their contributions, the publication of this book would not have been possible.

December 2016

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Solution in Energy: Energy End-Use Efficiency Based 100% Renewable Community Power

Tanay Sıdkı Uyar

Abstract

Solution in Energy is energy end use efficiency as a priority with which the size of the problem can be reduced. Countries with lower environmental standards have been a destination for the inefficient and polluting end-use technologies that are cast off, with the support of export credits, from more industrialized countries. Countries highly dependent on fossil fuels are in a position to face a heavy burden on their state budgets. The solution is to promote energy end-use efficiency by using the best available technologies and supply all of the energy needed with renewable energy, supported by renewable energy storage and smart grid technologies.

Keywords: Community Power, Energy End-Use Efficiency, 100% Renewable Energy,

Introduction

Human beings must come to a consensus regarding the sun's role in providing a living space for human beings on earth (see Fig 1). The world is like a cell surrounded by a blanket of greenhouse gases that give it an atmosphere with an average temperature of 16°C, in the middle of a space with an average temperature of -60°C (see Fig 2). Considering its natural solar, wind and biomass potential, world definitely has more renewable energy resources annually than the total fossil and uranium resources (see Fig 3, 4).

Energy Problem on this earth started during 1850s with the Industrial Revolution. Energy requirements of Industrial Revolution forced humanity to use coal extensively which ended up with mass casualties at the industrialized cities of the world (see Fig 5, 6).

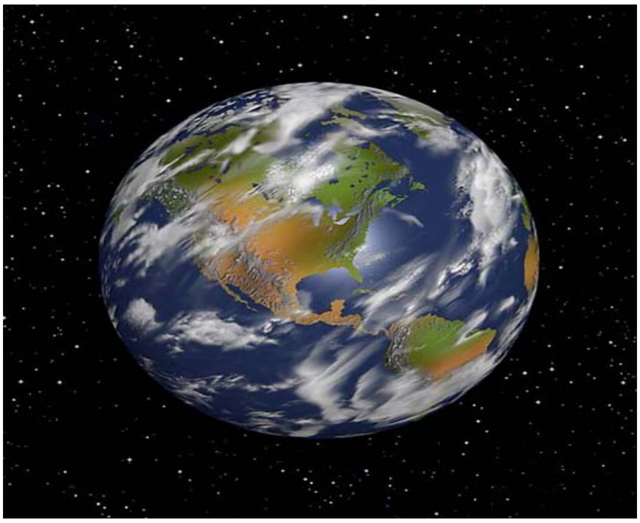


Figure 1. Our living space

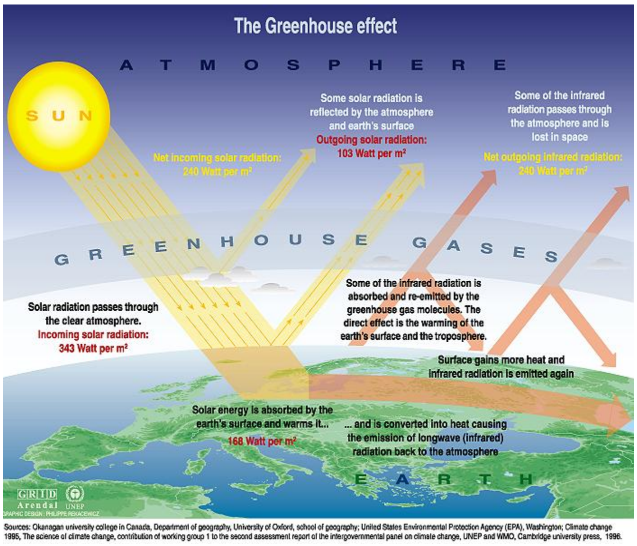


Figure 2. Sustainable energy supply of sun to our living space

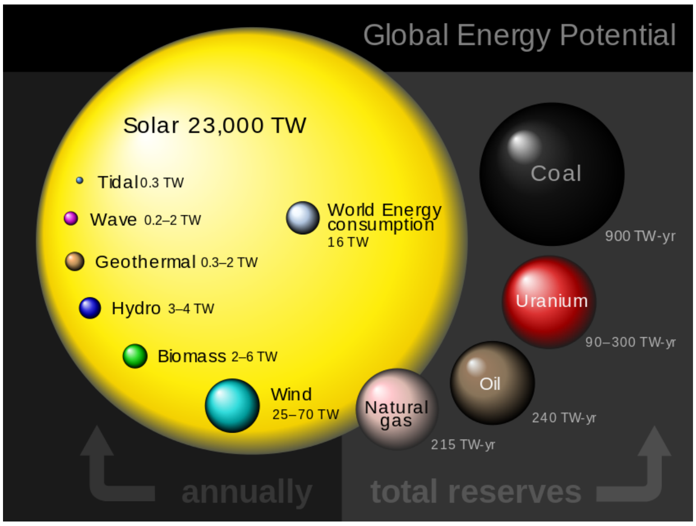
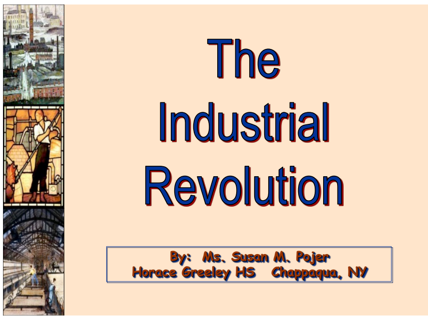


Figure 3. Comparison of total energy consumption on earth with the annual renewable energy resources, fossil and nuclear fuel reserves.

Figure 4. Renewable resources were available before, are available today and will be available in the future

Humanity has witnessed the death of about 4500 individuals as a result of the London Fog in 1952 due to the extensive coal combustion in London (Pojer, Susan M., 2017) (see Fig 7, 8). As a solution petroleum became popular and all the policies were adjusted accordingly to control the countries with petroleum resources. OECD countries using petroleum tried to control petroleum trade to protect themselves from the OPEC countries. With the petroleum crisis nature forced human beings to save energy without any other alternative available. IEA was established by OPEC countries to monitor politically the fight against OPEC countries.



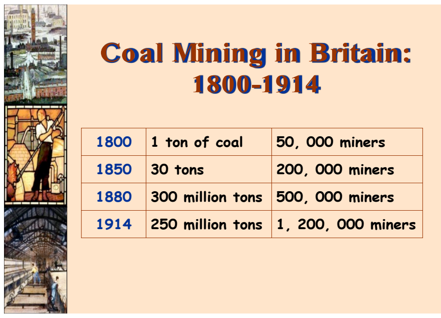


Fig. 5, 6, 7, 8: The polluted cities of UK as a result of coal combustion to supply energy need of the industrial revolution

Meanwhile the technology of nuclear weapon production facilities so called nuclear reactors were invented, designed and manufactured to dominate the world by super powers of the world between 1950s and 1970s. Petroleum crisis and commercially unavailable renewable energy technologies of today helped the owners of the nuclear weapon material producing nuclear reactors to convince the decision makers of that time to invest on nuclear power plants to use the waste heat produced during the process for solving the energy problems of the world. We have witnessed the construction of almost all of the nuclear reactors between 1973 and 1978.

After 1978 OECD countries who have practiced that the nuclear option is not working effectively, initiated technology agreements between Energy Ministries of OECD countries to develop safe nuclear, clean coal and renewable energy technologies. They have also initiated Technology Agreements on energy end use efficiency and local and national decision support tool development such as ETSAP (Energy Technology Systems Analysis Program).

To justify benefits of energy end use efficiency and renewable energy utilization and to demonstrate the environmental and health effects of conventional energy production and consumption on agricultural products, forests and human health became a topic to be investigated by environmental economists.

The externalities of energy consumption and production were not internalized globally. European countries beginning with Olaf Hohmeyer in Germany and David Pearce in UK initialized the social costs calculations in 1993 with EXTERNE project.

With the UNFCCC (United Nations Framework for Climate Change Convention) in 1994 signed with sufficient number of countries, fossil fuel combustion even with clean coal technologies became obsolete. Safe nuclear did not convince anybody on earth after Chernobyl and Fukushima nuclear accidents. Decommissioning time of the existing nuclear reactors arrived and now we understand that cradle to grave costs of nuclear power plants are too high to afford for any country on earth. We have started to hear that Global Nuclear Energy Partnership was designed by nuclear powers to shift some of the nuclear waste recycling and storage facilities to countries who are willing to host nuclear facilities in their countries. We have heard that 4th International Nuclear Decommissioning and Nuclear Waste Management Conference will take place in UK on 1 March 2017.

Problem

We know that up until the 1850s, human activities were carried out in substantial harmony with nature. The local damage caused by human activities was rarely irreparable and did not overstep the limits of the natural carrying capacity. Beginning in the 1850s, rising energy demand driven by the industrial revolution forced humanity to start consuming more fossil fuels. During the 1950s, thousands of people died from respiratory problems due to coal burning in the big cities of the world. As a result, “clean coal technologies” were devised to prevent such deaths. Burning coal with fewer externalities became one of the options for the future of the energy industry. After the Rio Conference in 1992, when it was acknowledged that the real threat to the atmosphere is the global warming caused by fossil fuel combustion, the arguments for clean coal combustion became obsolete.

According to Sierra Club,”the 100000-MW milestone was surpassed when Houston-based Dynegy announced it will retire 1877 MW of coal-fired power assets, phasing out Units 1 and 3 at its Baldwin Power Station and Unit 2 at its Newton Power Station, both in Illinois.”(Power-Eng., 2017) Nick Engelfried from greenanswers.com reported that a new coal power plant near Purdue University, canceled in February 2011 and presented in Table 1, “was the 150th new coal plant to be cancelled since then-Vice President Dick Cheney unrolled plans to build a new fleet of coal-fired power plants in 2001.” (Engelfried, Nick, 2017) The Chinese authorities have halted construction on 30 large coal-fired power plants with a combined capacity of 17 GW (see Fig 9).(Cleantechnica, 2017)

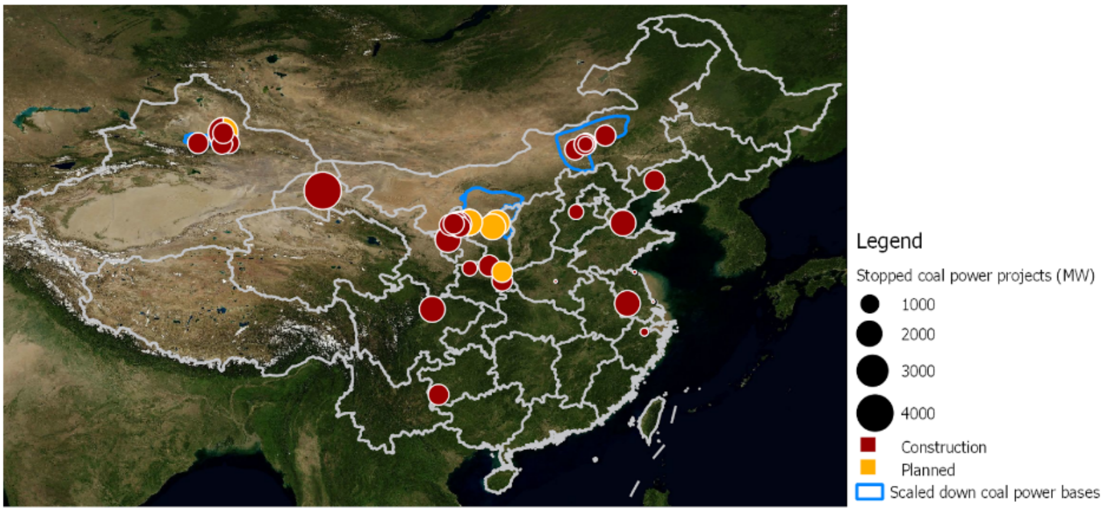


Fig. 9: Scaled down coal power bases and stopped coal power projects in China

The global coal boom has started to slow, a new report says, as more plans for new power plants are now being shelved than completed (Carbonbrief, 2017).

Table 1. Proposed global coal-fired generating capacity 2014 by region (megawatts).

Region	Halted (Shelved or Cancelled)	Completed	Ratio of Halted to Completed
East Asia	194 625	227 650	1:1
South Asia	313 420	80 340	4:1
Europe/Turkey	96 600	14 599	7:1
United Stated and Canada	23 653	14 677	2:1
Southeast Asia	22 260	13 701	2:1
Latin America	17 890	4 016	4:1
Other	41 504	1 883	22:1
World Total	709 952	356 866	2:1

Source: Global Coal Plant Tracker, January 2015

The 1970 petroleum crisis convinced the energy decision-makers that dependence on petroleum is not a wise energy strategy. The first solution that human beings naturally adopted under those circumstances was using less energy than before. Countries that learned from this have initiated energy end-use efficiency programs, which ended up generating some of today's best available technologies. They consume ten times less energy than technologies of the 1970s, but provide the same transportation, industrial, and residential services. In

1973, the decision-makers were convinced that the waste heat from nuclear weapon production facilities could be a way to supply the total energy requirements of the world. The majority of the existing nuclear power plants were built during this period. After the Three Mile Island nuclear disaster in 1978, the United States was the first country where plans to build new nuclear power plants were stopped. Approximately 100 nuclear power plants that had been ordered between 1973 and 1978 were also canceled. The main argument behind these actions was explained by Mark Halt: "No nuclear power plants have been ordered in the United States since 1978, and more than 100 reactors have been canceled, including all ordered after 1973. The most recent U.S. nuclear unit to be completed was TVA's Watts Bar 1 reactor, ordered in 1970 and licensed to operate in 1996. Reasons for the 30-year halt in U.S. nuclear plant orders include high capital costs, public concern about nuclear safety and waste disposal, and regulatory compliance costs." (Holt, M., 2009)

Steps taken Towards the Solution

Beginning in the 1970s, the OECD countries started trying to define the energy problem and find feasible solutions to it. In 1974, to counter the Organization of the Petroleum Exporting Countries (OPEC), OECD countries established the International Energy Agency (IEA) as a political union of rich countries that would take measures such as ensuring a mandatory three-month store of petroleum in each country. The IEA decided also to initiate 40 multilateral technology initiatives (Implementing Agreements) for facilitating energy technology cooperation between the scientists and researchers of OECD countries. (Implementing Agreements on technologies such as bio-energy, geothermal energy, photovoltaic power systems, renewable energy technology deployment, solar heating, and cooling and wind energy systems contributed a lot to the research, development, and commercialization of renewable energy technologies. (IEA, 2017)

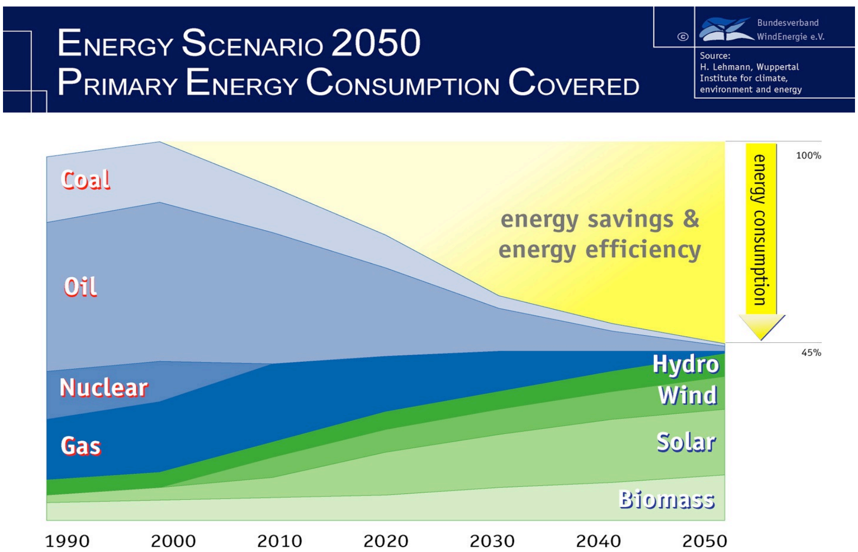


Figure 10. Targets of Germany for 100% renewable energy usage by 2050

A typical plan from H. Lehmann, Wuppertal Institute for climate environment and energy published by Bundesverband Windenergie e.V., Germany targeting 100% renewable energy usage by 2050 and energy demand decrease targeted in different sectors can be seen in the figures below (see Fig 10, 11).

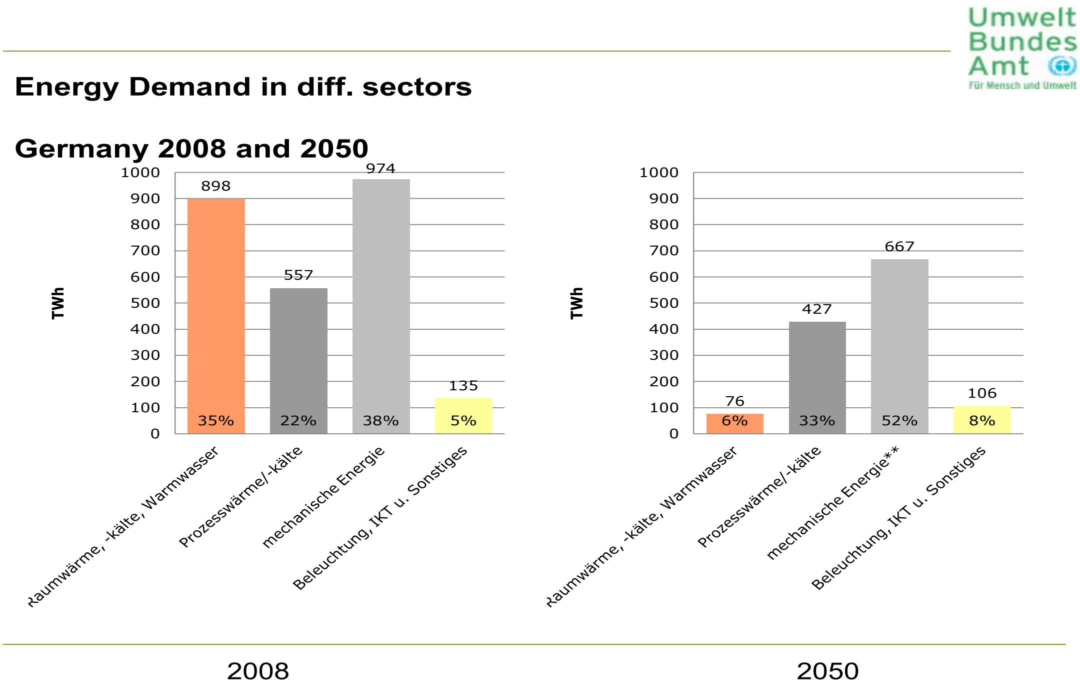


Figure 11. Energy demand decrease targets in different sectors of Germany

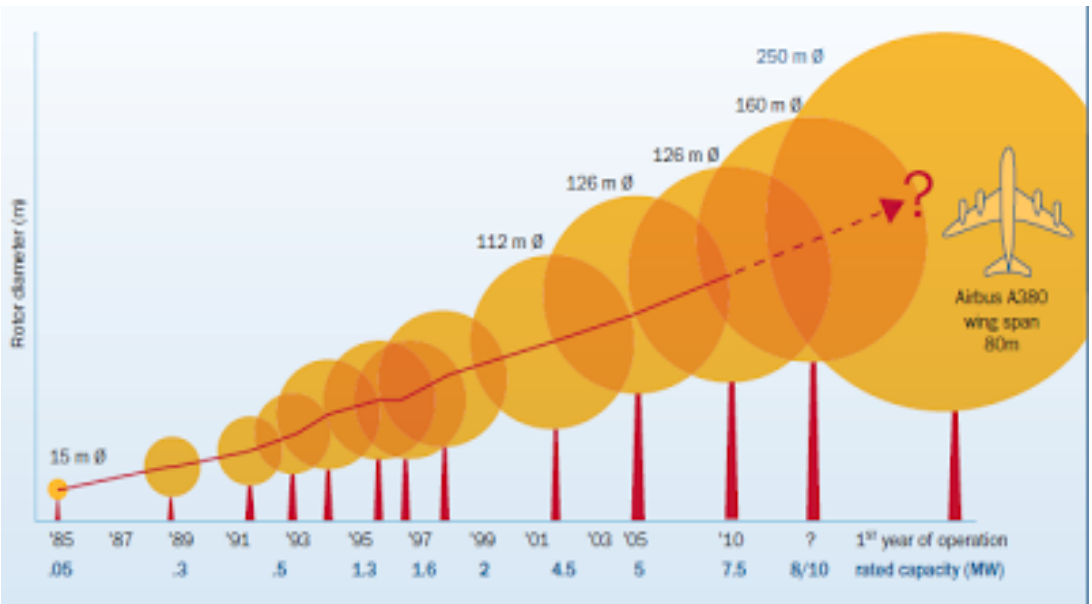


Figure 12. Wind turbine technology development

Technological research and development efforts accelerated after 1980 in industrialized countries, expediting the development of renewable energy technologies. Supporting wind power with tax credits contributed greatly to the establishment of a market for wind turbines in the U.S. After 1996, we saw Germany and the European Union give huge support to megawatt-scale wind turbine commercialization. Today, we know of 10MW prototype production efforts in the U.S. (Next Big Future, 2017) (see Fig 12).

The European Union, making use of the existing experience of Denmark and Netherlands on renewable energy, has followed Germany. In March 2007, the EU's leaders endorsed an integrated climate and energy policy that aims to combat climate change and increase the EU's energy security while strengthening its competitiveness. They committed Europe to transforming itself into a highly energy-efficient, low carbon economy. To kick-start this process, the EU heads of state and government set a series of demanding climate and energy targets to be met by 2020, known as the "20-20-20" targets (EC Europa, 2017). These are: 1. A reduction in EU greenhouse-gas emissions of at least 20% below 1990 levels 2. 20% of EU energy consumption to come from renewable resources 3. A 20% reduction in primary energy use compared with projected levels, to be achieved by improving energy efficiency. The targets for 2030 is more improved up to 40%, 27% and 27 % respectively (see Fig 13). An important result of this development was the 8.1 million people working in the renewable energy industry globally at the end of 2015 (see Fig 14).

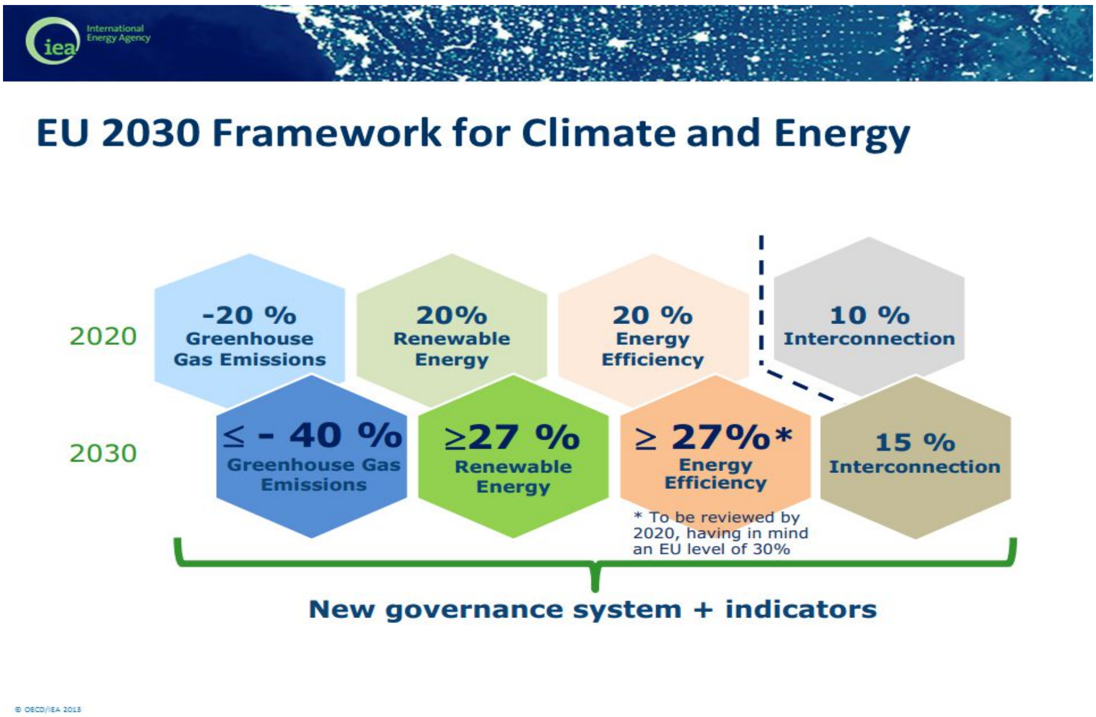


Figure 13. EU 2030 framework for climate and energy

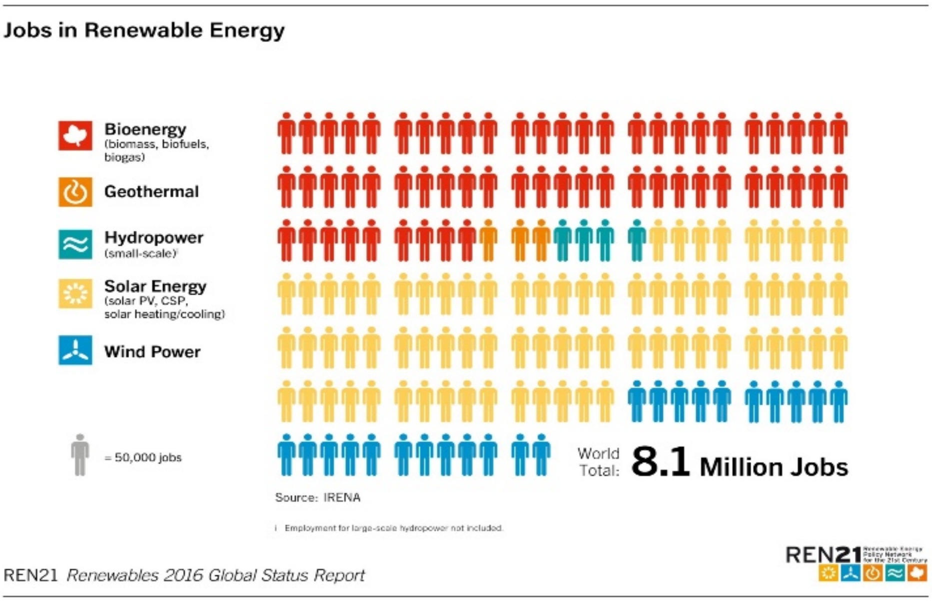


Figure 14. Global jobs in renewable energy

Wind power global capacity has reached to 433 GW with leading countries as China, USA, Germany and India at the end of 2015. Solar PV global capacity has reached to 227 with leading countries as China, Germany, Japan and USA at the end of 2015 (see Fig 15, 16, 17, 18).

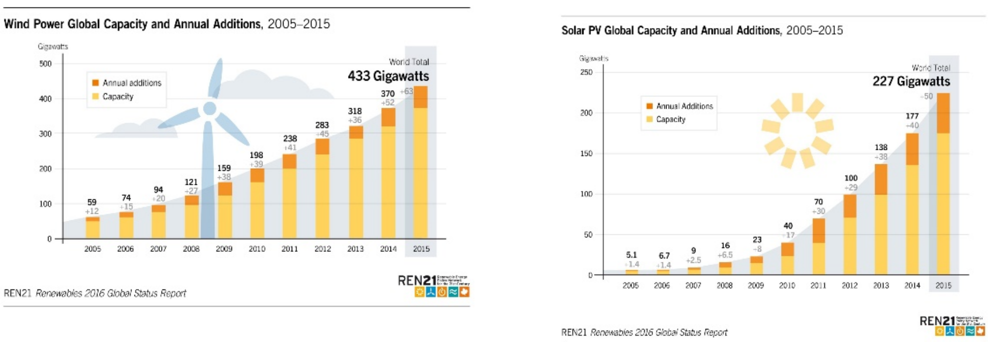
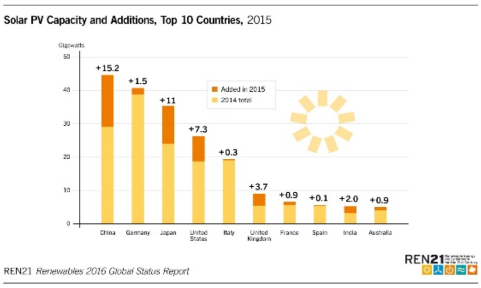


Figure 15, 16. Wind power and solar PV global capacity and annual additions (2005-2015)



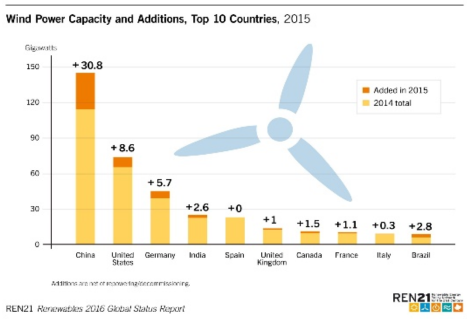


Figure 17, 18. Wind power an solar PV capacity and additions top 10 countries 2015

Today coal is becoming more cheap and readily available in the market as the local and global externalities of coal burning in the atmosphere become more apparent (see Fig 19).

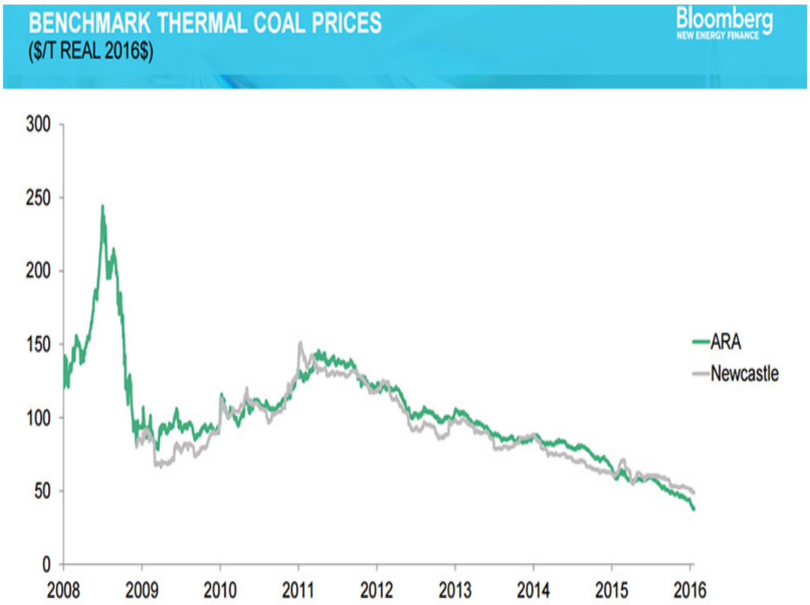


Figure 19. Bench mark thermal coal prices

Investments in newer, renewable technologies tend to stop large-scale projects and promote decentralized alternatives. This contradicts the marketing bias toward large-scale projects. To justify the necessity of large-scale projects, the implementation of energy end-use efficiency and renewable energy technologies is consistently delayed. The existing distribution networks are designed for large-scale, centralized power plants. The main barrier to the full implementation of renewable energy technologies in many countries is the unwillingness of the energy transmission authority to redesign the grid so that it can accept more of the decentralized energy produced. Long-term estimates for the energy mix of the world demonstrate that renewable energy utilization is inevitable, as shown in the figure below (see Fig 20). The question today is, which countries will be in which part of the picture. Department of Energy in USA declared that renewable energy revolution started (see Fig 21).

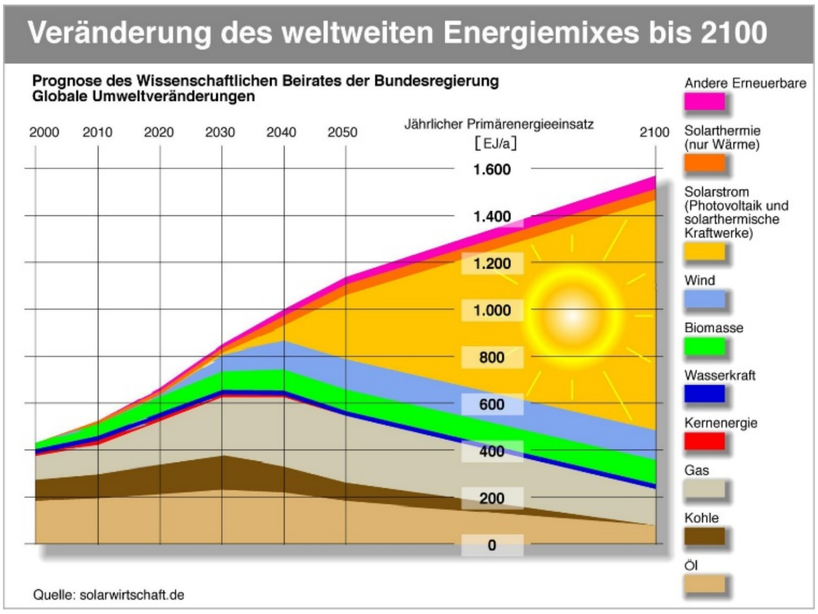


Figure 20. Changes in the global energy mix to 2100

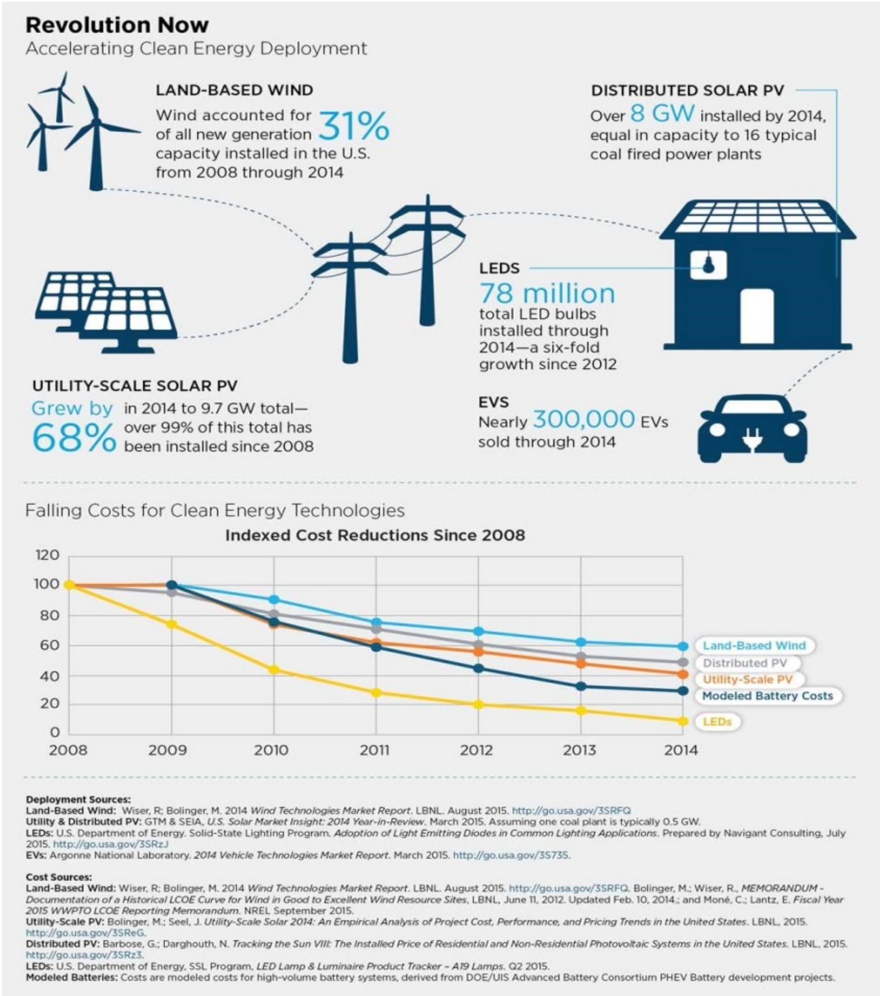


Figure 21. Revolution Now: Accelerating clean energy deployment at USA

The decrease in on shore wind levelised cost ($/MWh) and solar pv module cost ($/W) can be seen from wind and solar experience curves given in figure 22.

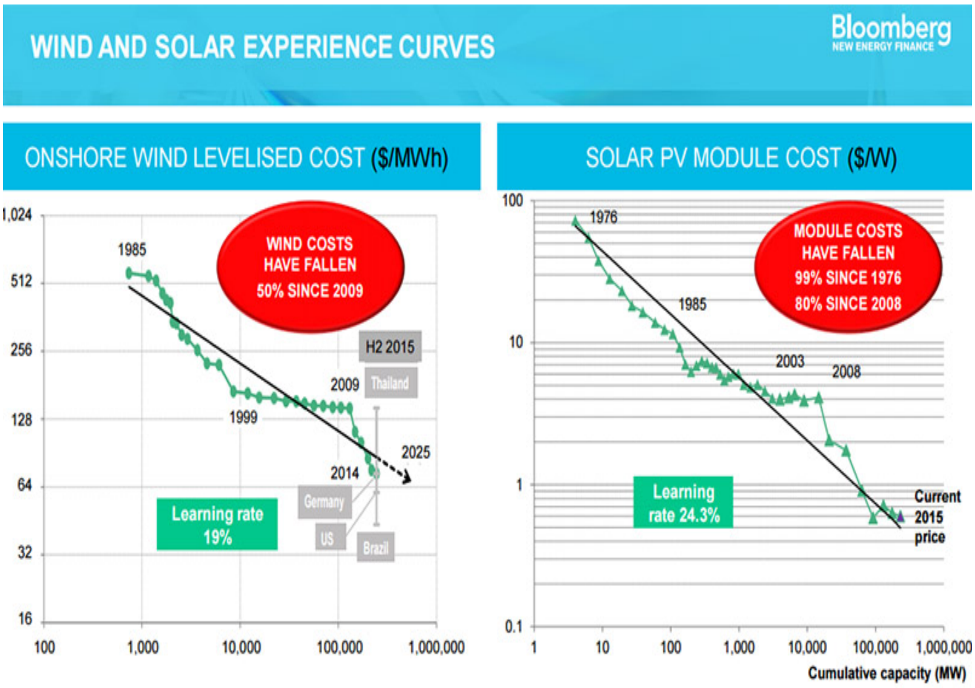


Figure 22. Wind and Solar experience curves

Danish renewable energy developer Pure & Better Energy awarded 20 MW of solar PV capacity in latest cross-border auction for cost of DKK 12.89/MWh (PV Magazine, 2017) (see Fig 23) IRENA study shows globally prices of utility –scale solar PV in key markets.

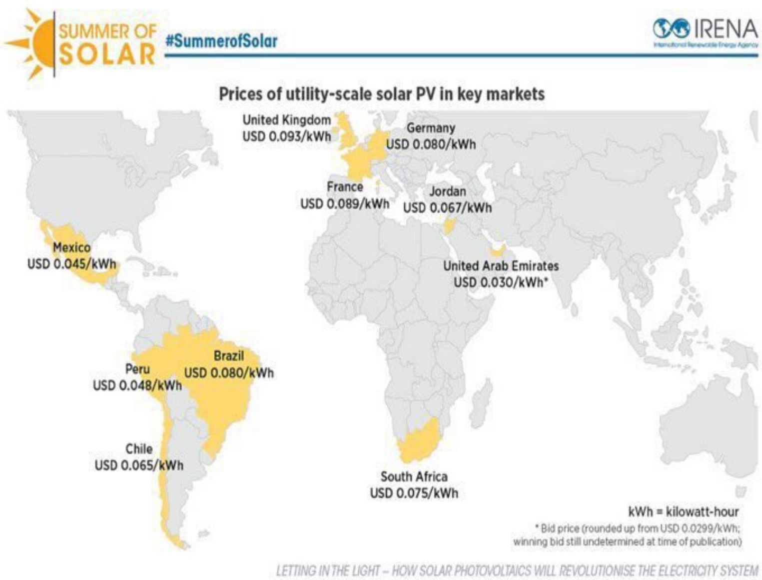


Figure 23. Prices of utility-scale solar PV in key markets

Solar farm costs are shrinking and solar and wind generated electricity is becoming the cheapest electricity on earth in 10 years (see Fig 24, 25).

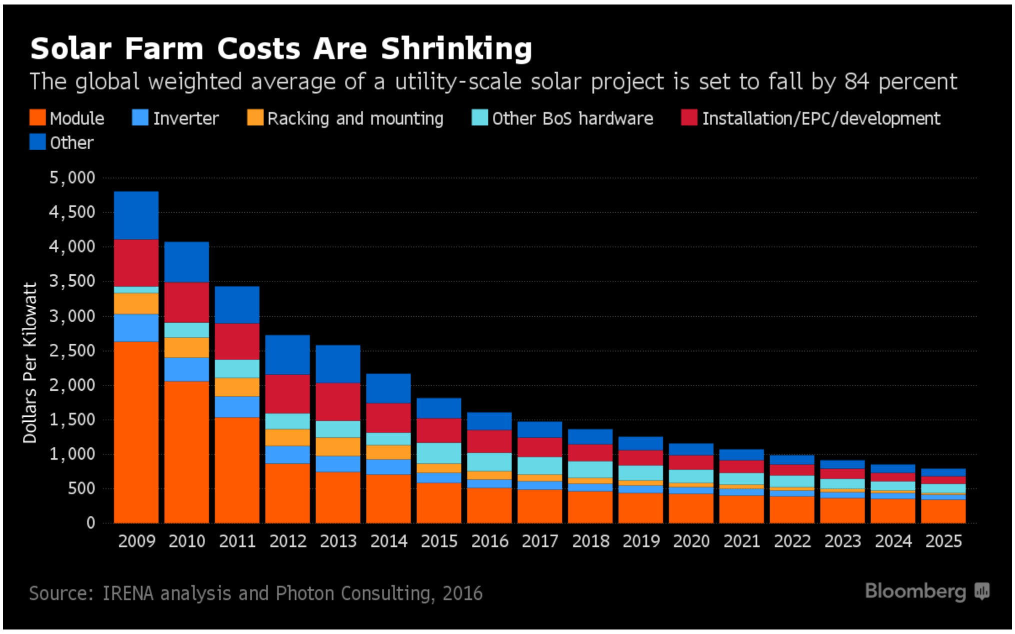


Figure 24. Solar farm cost according to years

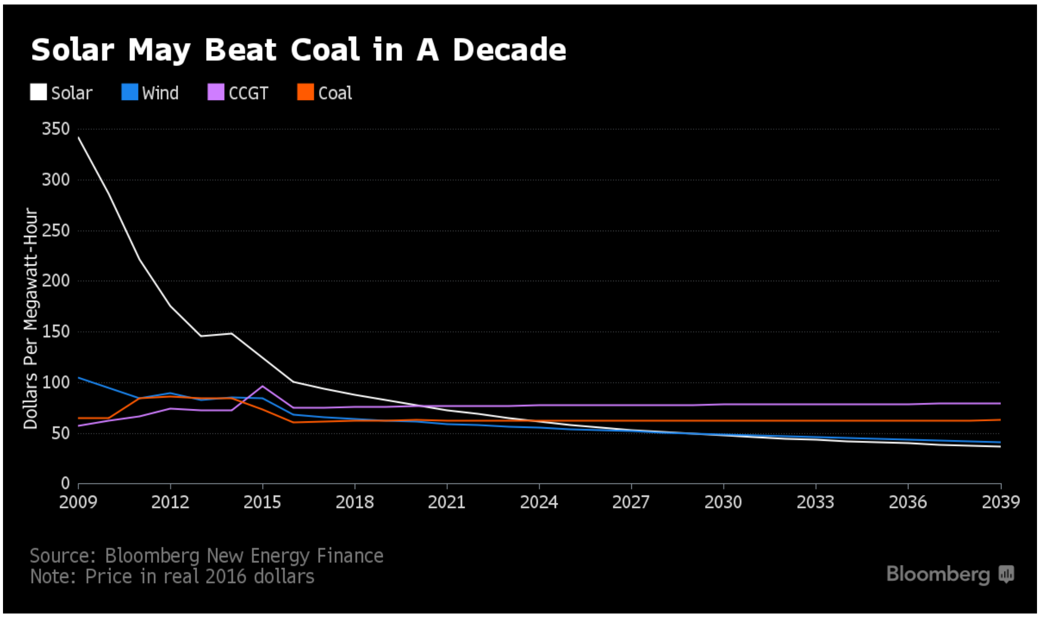


Figure 25. Predicted prices for solar, wind, CCGT and coal

In Turkey, we have organized four workshops together with the energy committee of the Young Businessmen's Association of Turkey (TÜGİAD), inviting all actors in Turkey's energy sector. The final report, entitled "Energy Problems of Turkey and Suggested Solutions", included all the agreed upon recommendations of the workshop participants (Uyar, T.S., 2004). Through Renewable Energy Association of Turkey (EUROSOLAR Turkey) we are making our contributions by organizing an annual International 100% Renewable Energy Conference (IRENEC), since 2000 to set up an international platform to discuss the technical, economic, political, and administrative aspects of this monumental transition from fossil fuels to renewable energy sources, and to contribute to the 100% renewable energy goal without using nuclear energy or carbon-capture technology. IRENEC conferences aim to pursue improvements in energy end-use efficiency and renewable energies, and to create the infrastructure required to realize the 100% renewable goal in industry, local communities, architecture, and transportation (IRENEC, 2017). It is now time to speed up the global transition to 100% renewable energy (see Fig 26).

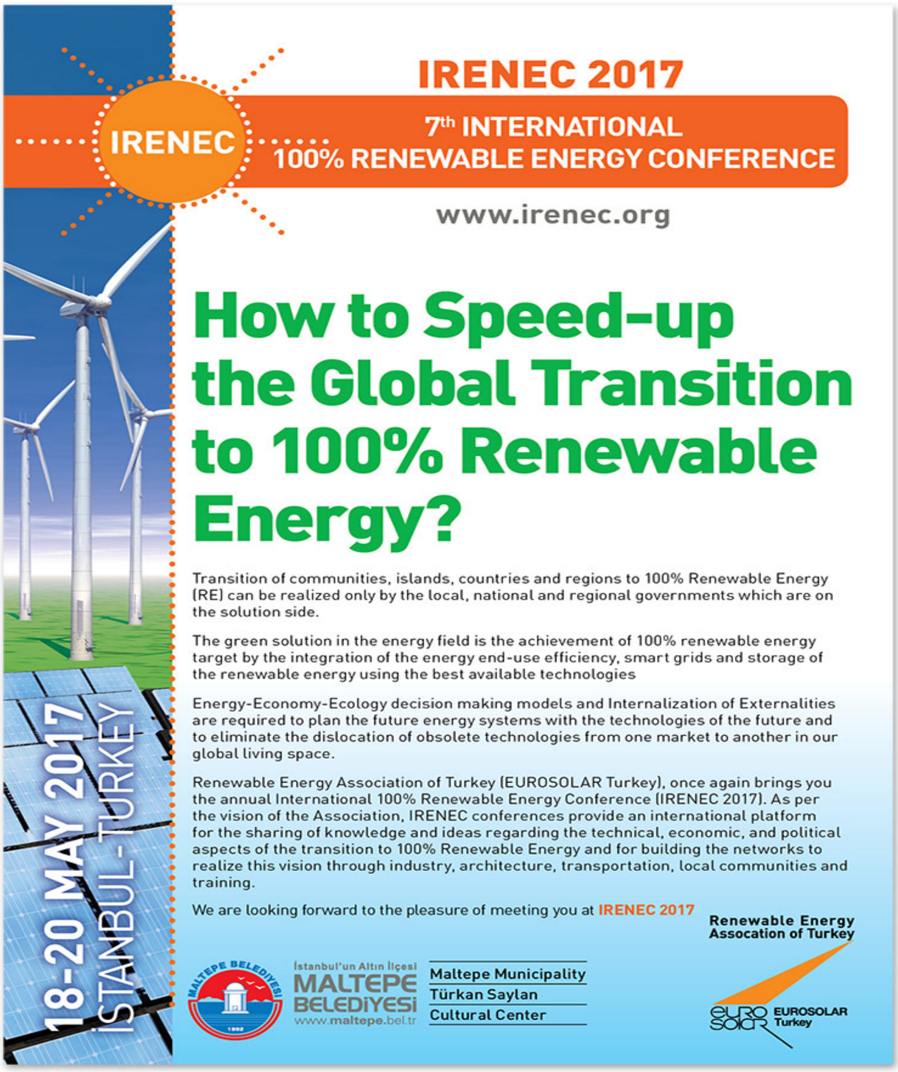


Figure 26. Call for paper for IRENEC 2017

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2

Prediction of Renewable Energy Consumption in Turkey Using Artificial Neural Networks

Ayşe Ayçim Selam
Ahmet Kubilay Atalay
M. Övül Arıoğlu Akan

Abstract

Due to the concern for sustainability, renewable energy sources have become the fastest growing source of world energy. Turkey, as a developing country which imports over 70% of its primary energy supply, is in the middle of different climates enabling the use of a variety of these sources. Therefore, the government provides support tools, including fiscal incentives and public finances to promote wide use of renewable energy. The development of effective renewable energy policies requires reliable consumption data. In this paper, renewable energy consumption in Turkey is predicted using Artificial Neural Networks. The renewable energy indicators (some of which are total primary energy supply, electricity consumption, electricity production, energy imports, gross domestic product, population etc.) are evaluated as independent variables using historical data from 1990 to 2012. The results indicate that Artificial Neural Networks is a powerful technique in energy demand forecasting as stated by similar studies in the literature.

Keywords: Renewable energy, Renewable energy consumption, Prediction, Artificial neural networks

Introduction

Renewables, excluding large hydro, accounted for 9.1% of world electricity generation in 2014, up from 8.5% in 2013, with a corresponding increase of 17% in global investment ($270.2 billion invested in 2014 in renewable power and fuels excluding large hydro-electric projects)(McCrone, 2015). They have become the fastest growing source of world energy with their share of electric power generation increasing from 10%–15% in 2010, while the fossil fuel sources grew 3% or 4% (EIA, 2012). The reason behind this is the concern for sustainability resulting from factors, including but not limited to, the depletion of natural resources, life-threatening levels of pollution, global warming, climate change and the ever-increasing worldwide energy consumption (Komor & Bazilian, 2005; Apergis & Payne, 2010).

The Renewable Energy Working Party of the International Energy Agency (IEA) defines renewable energy as follows: "Renewable Energy is derived from natural processes that are replenished constantly. In its various forms, it derives directly or indirectly from the sun, or from heat generated deep within the earth. Included in the definition is energy generated from solar, wind, biofuels, geothermal, hydropower and ocean resources, and biofuels and hydrogen derived from renewable resources" (IEA, 2013a).

In line with the above definition, renewable energy sources can be classified under the following categories (IEA, 2013a):

- Hydroelectricity
- Geothermal
- Solar
- Tide / Wave / Ocean
- Wind
- Solid biofuels, biogases, liquid biofuels
- Renewable municipal waste

As is the case with other developing countries; the energy consumption in Turkey is constantly increasing due to the economic developments, population growth, increasing urbanization and industrialization (Öztürk, Bezir, & Özek, 2009; Kotcioğlu, 2011), and thus, it is in a position to import over 70% of its primary energy supply (with oil and natural gas having the biggest shares) (Kaya & Kılıç, 2012). On the other hand, Turkey has a substantial amount and wide range of renewable energy sources, and it is located in an advantageous geographical position that enables their effective utilization (Barış & Küçükali, 2012; Benli, 2013; Yüksel & Kaygusuz, 2011). Moreover, the primary energy production is increasing and the most significant developments are observed in hydropower, geothermal, solar energy and coal production (Yüksel & Arman, 2014). Despite these developments, the share of renewable energy in electricity generation was only 17.4% by the end of 2008 (Yüksel, 2013). The renewable energy potential in Turkey (hydropower, solar, biomass and wind power) is sufficient to meet the accelerated demand (Kotcioğlu, 2011), but it has not been efficiently utilized, leaving the country with an urgent need for effective energy policies.

Due to the above-stated reasons, energy efficiency has become a significant issue in the government's agenda. Hence, since 2005, the Turkish Government has taken steps to improve the energy efficiency and develop renewable energy sources (RES), among which are the Law on Utilization of RES for the Purpose of Generating Electrical Energy (2005), the Energy Efficiency Law (2007), accession to the International Renewable Energy Agency (IRENA) in June 2009, the adoption of the Ministry of Energy and Natural Resources (MENR) Strategic Plan (2010–2014) and the Energy Efficiency Strategy Paper published in February 2012 (IEA, 2013b; ECS, 2014). Turkey's energy policies mainly include meeting demand as much as possible through indigenous resources, diversifying energy supplies and avoiding dependence on a single source or country and adding new and renewable sources (geothermal heat, solar, wind, etc.) as soon as possible to the energy supply system (Öztürk, Bezir, & Özek, 2009).

The development of effective renewable energy policies requires reliable consumption data. Thus, the aim of this study is to predict the renewable energy consumption in Turkey using Artificial Neural Networks (ANN). Artificial networks, which can be defined as information-processing systems that have common performance characteristics with biological neural networks, have been developed as "generalizations of mathematical model of human cognition" (Kialashaki & Reisel, 2014). Ahmad et al. (2014) have categorized the most widely used methods for forecasting building energy consumption into three groups, which are Engineering, Statistical and Artificial Intelligence (AI) methods. They have identified ANNs as the most commonly implemented method. Among the advantages of ANNs, which they have pointed out are the following (Ahmad et al., 2014):

- The ability to execute tasks that linear programs cannot;
- A parallel nature enabling them to carry on working when an element fails;
- The ability to learn and not needing to be programmed;
- The fact that they can be executed in any application.

The ANN technique has been reported as a reliable and powerful technique in energy demand forecast (Kialashaki & Reisel, 2014). The independent variables in the present model are the renewable energy indicators including but not limited to total primary energy supply (TPES), electricity consumption, electricity production, energy imports, gross domestic product (GDP) and population.

Artificial Neural Network Application

The researchers used different methods and indicators to evaluate governments and their policies on renewable energy. Some methods used in evaluation of renewable energy are:

- Data envelopment analysis (Chien & Hu, 2007; Wang et al., 2012),
- Granger causality tests (Apergis & Payne, 2010; Jinke, Hualing, & Dianming, 2008; Nazlioğlu, Lebe, & Kayhan, 2011),
- Empirical studies, interviews (Hirschl, 2009; Martins & Pereira, 2011; Nagy & Körmendi, 2011),

- General evaluations (Barış & Küçükali, 2012; Valentine, 2011),
- Other (Liddle, 2012; Reuter et al., 2012), etc.

Escrivá-Escrivá et al. (2011) proposed an adaptive algorithm based on ANNs for the short-term prediction of total power consumption in buildings with several independent processes. The model, which is able to adjust a load curve for a particular facility and use it to predict the power consumption for the other days, was used to predict the whole consumption expressed as 96 active energy quarter-hourly values of the Universitat Politècnica de València with very accurate results. The consumption forecasts were obtained from the prediction of each end-use of the total consumption. This model was later upgraded by Roldán-Blay et al. (2013) by using a time temperature curve forecast model. The new model, which was validated with the consumption forecast of the Universitat Politècnica de València for an entire year, improved the relationship between expected consumption and temperatures. However, the authors state the fact that it requires more information to make a consumption forecast than the previous method.

Ahmad et al. (2014) reviewed the building electrical energy forecasting method using AI methods such as support vector machine (SVM) and ANN, which led them to the conclusion that the hybrid approach using these two forecasting methods promises more accurate results. Oğcu et al. (2012) compared the performance of Support Vector Regression (SVR) model, which is an extended version of SVM used for general estimation and prediction problems, and ANN for predicting electricity output in Turkey within 2010 and 2011. They showed that although both methods perform well, seasonal SVR slightly outperforms ANN in terms of forecasting the real consumption, which they stated to be consistent with Mean Absolute Percentage Error (MAPE) results of the training data.

In this study, ANN is used for prediction of renewable energy use in Turkey. For this purpose, a set of input variables are selected. These are provided from energy evaluating articles. Here, unit and definition about the selected variables are referred from the World Bank & International Energy Agency. Apart from that information, literature is surveyed with the aim of analyzing how the selected indicators are used for energy evaluation.

In the model, renewable energy consumption is the output variable and provided by the share in total final energy consumption. The TPES is the most frequent and basic indicator used to evaluate energy among researchers. This value is calculated by (TPES = Indigenous production + imports - exports - international marine bunkers - international aviation bunkers +/- stock changes) (World Bank, 2014). In other words, this value provides a country's energy usage.

One of the electric-related indicators is electricity consumption which is obtained by (Gross production + Imports - Exports – Losses). Natural gas is an important source of energy in Turkey, especially in heating, therefore in this study electricity production form natural gas is added to the model as an input variable.

Table 1. Variables of the ANN Model

IndicatorCode	IndicatorName	VariableType	Unit	Definition
RenewConsm	Renewable energy consumption (% of total final energy consumption)	Output	%	Renewable energy consumption is the share of renewable energy in total final energy consumption.
TPES	Total Primary Energy Supply	Input	Mtoe	Consists of: Indigenous production + imports - exports - international marine bunkers - international aviation bunkers +/- stock changes
ElecCons	Electricity Consumption	Input	TWh	Gross production + Imports - Exports - Losses
ElecProdNatGas	Electricity production from natural gas sources (% of total)	Input	%	Sources of electricity refer to the inputs used to generate electricity. Gas refers to natural gas but excludes natural gas liquids.
ElecProdHydro	Electricity production from hydroelectric sources (% of total)	Input	%	Sources of electricity refer to the inputs used to generate electricity. Hydropower refers to electricity produced by hydroelectric power plants.
ElecProdRenew	Electricity production from renewable sources, excluding hydroelectric (% of total)	Input	%	Electricity production from renewable sources, excluding hydroelectric, includes geothermal, solar, tides, wind, biomass, and biofuels.
EnergyImp	Energy imports, net (% of energy use)	Input	%	Net energy imports are estimated as energy use less production, both measured in oil equivalents.
EnergyIntensity	Energy intensity level of primary energy	Input	(MJ/$2011 PPP GDP)	Energy intensity level of primary energy is the ratio between energy supply and gross domestic product measured at purchasing power parity.
GDPPPP	GDP, PPP	Input	constant 2005 international $	GDP, PPP is gross domestic product converted to international dollars using purchasing power parity rates.
Population	Population	Input	(millions)	Total population is based on the de facto definition of population, which counts all residents regardless of legal status or citizenship.

The statistical data used is collected from World Bank (2014) & IEA (2014) for Turkey between 1990-2012.

The highest percentage of electricity production is achieved by hydroelectric sources in Turkey, so electricity production from hydro and other renewables are evaluated as two separate input variables in the model.

Energy imports are attained in percentage by (energy use – energy production). Energy intensity is an indication of how much energy is used to produce one unit of economic output (World Bank, 2014). The lower this ratio is the less energy is used to produce one unit of output. The two final input variables are GDP, PPP as an economic indicator and population as a social indicator. In Table 1 below, the list of variables is provided with their unit and definitions.

In the first step of the prediction, an ANN with a single hidden layer is used. The data is randomly separated by %60, %20 and %20 for training validation and test respectively. The number of neurons in the hidden layer is varied from 2 to 20 in order to find the optimum number of neurons for the best prediction performance. Levenberg-Marquart algorithm is used for training of ANN. Stopping parameters are given in Table 2.

Table 2. Stopping Parameters

Parameter	Value
Maximum # of epochs to train	50
Performance goal	0
Maximum validation failures	50
Minimum performance gradient	1e-10

The method is quite coincidental so training procedure of each ANN architecture is repeated 500 times and averages of mean squared errors and correlation of test data are calculated for a fair comparison in the determination of optimum number of neurons in hidden layer. The averages of the mean squared error values of training, validation and test data and correlation of test data for each ANN architecture is provided as a performance index in Table 3.

It can be seen from Table 3 that, an ANN with 9 neurons figures out best prediction performance. Average mean squared error of test data is lowest and average correlation is high as well, which means that coefficient of determination is high in this architecture. In addition to that the performance index exhibits that the average mean squared error of test data is increasing while average mean squared error of train data is decreasing with respect to an increase in number of neurons in hidden layer with a hidden layer size greater than 9 neurons. At this point it can be stated that an ANN with a hidden layer size greater than 9 neurons is not learning but memorizing. For this reason, an ANN with more neurons in hidden layer is not investigated.

Table 3. Performance Index

Hidden Layer Neurons	Average MSE train	Average MSE validation	Average MSE test	Average correlation test
2	0.8516	1.2108	2.0871	0.9387
3	0.6469	1.1218	2.0871	0.9561
4	0.6782	1.0718	1.9645	0.9625
5	0.9343	0.9651	1.8273	0.9618
6	0.4960	0.9792	1.5312	0.9672
7	0.3853	1.1056	1.4579	0.9679
8	0.3590	1.1246	1.6806	0.9705
9	0.3100	1.0544	1.4127	0.9703
10	0.2885	1.2506	1.6648	0.9606
11	0.3033	1.2837	1.7621	0.9650
12	0.3362	1.5755	1.9555	0.9612
13	0.3253	1.5979	1.8524	0.9627
14	0.4066	1.7623	2.1893	0.9549
15	0.3777	1.9177	2.2228	0.9501
16	0.3504	2.2628	2.1366	0.9519
17	0.2586	1.9983	2.3682	0.9557
18	0.5874	2.2632	2.8486	0.9412
19	0.4453	2.2994	2.6908	0.9494
20	0.3885	2.6914	3.3061	0.9367

The size of the hidden layer is determined as 9 in the first stage. Beyond this point the second stage is focused on the acquisition of the best ANN with 9 neurons in hidden layer. The final architecture of the proposed ANN is given in Figure 1.

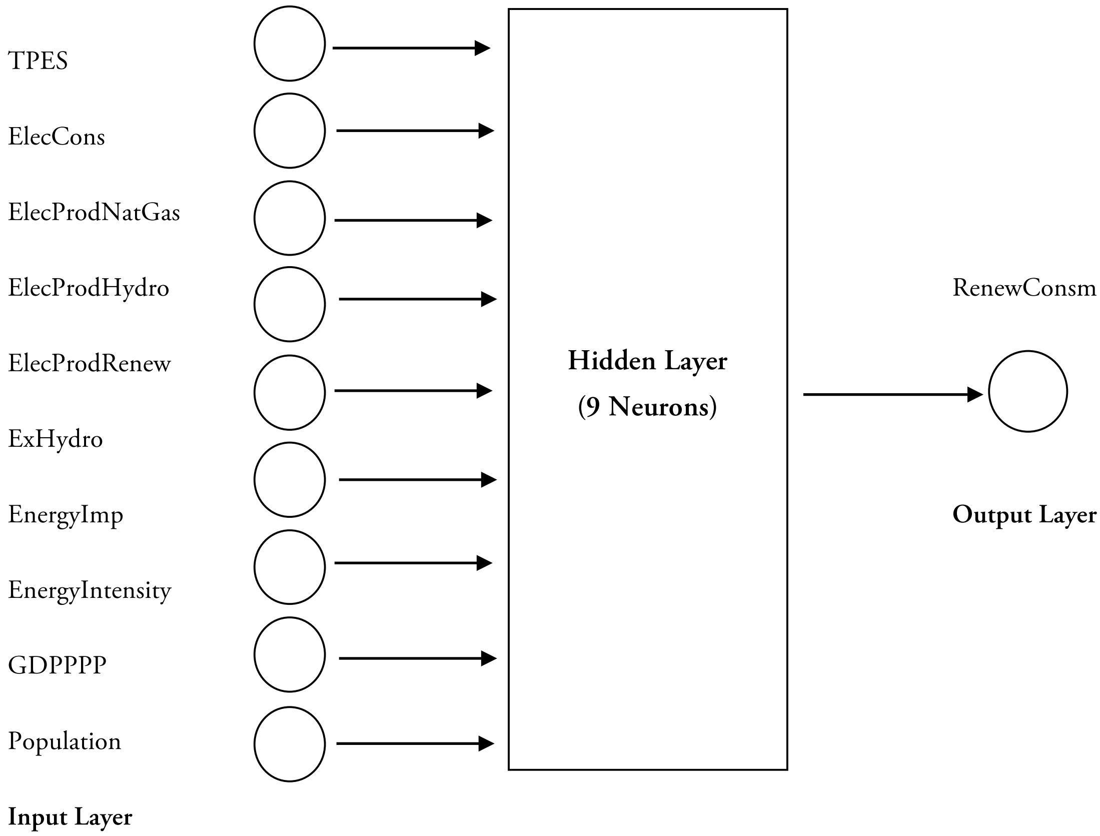

Figure 1. Proposed ANN Architecture (adapted from Bagnasco et al., 2015)

In the second step an ANN with 9 neurons is trained for 1000 times with same stopping parameters mentioned in the first step. Among these trials the ANN with best prediction performance is determined. The results are given as a performance index in Table 4.

Table 4. Performance Index

MSE train	MSE validation	MSE test	Correlation test
5.0973e-10	1.0810	0.0228	0.9997

It is traced that an ANN with 9 neurons exhibited highly accurate results in prediction. In Figure 2 observed versus predicted renewable energy consumption values are given graphically with coefficient of determination.

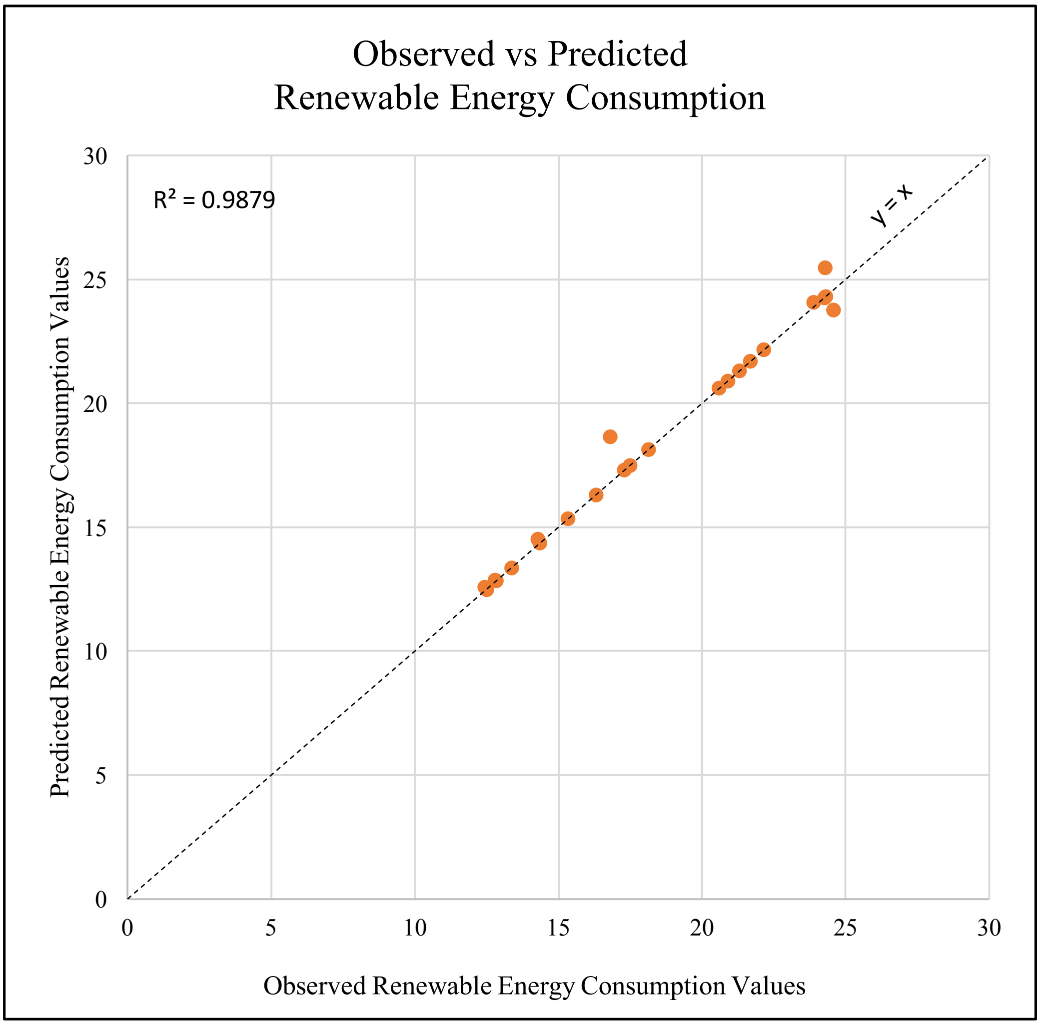

Figure 2. Observed vs Predicted Renewable Energy Consumption

Conclusion

One way to provide a clean environment for the future generations is to promote the usage of renewable energy sources and development of renewable energy technologies. Long-term initiatives are also a source of motivation for governments to use renewable energy. The development of renewable energy policies to be used for this purpose requires reliable consumption data. In this study, an ANN has been developed for the prediction of renewable energy consumption using historical data between 1990-2012. The output variable renewable energy consumption is predicted using the input variables TPES, electricity consumption, electricity production (from natural gas, hydro and renewable sources excluding hydro), energy imports, energy intensity, GDP and population. It is determined that an ANN with 9 neurons predicted renewable energy consumption with accurate results. The future of the study can focus on prediction by using hybrid algorithms comparative evaluation. Thus, this study provided similar results with the existing literature in that

ANN is a powerful technique in energy demand forecasting. A future research area for this particular study is comparing ANN with certain other methods used in energy demand forecasting such as ANFIS, Multiple Linear Regression. Moreover, the use of hybrid models, combining ANN with SVM, for example, is a promising research area in this field.

Nomenclature

AI	artificial intelligence
ANN	artificial neural networks
GDP	gross domestic product
IEA	International Energy Agency
IRENA	International Renewable Energy Agency
MAPE	mean absolute percentage error
MENR	Ministry of Energy and Natural Resources
RES	renewable energy sources
SVM	support vector machine
SVR	support vector regression
TPES	total primary energy supply

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3

Environmental Remediation Cost of Industrial Solid Waste in Terms of Extended Exergy

Candeniz Seçkin

Abstract

The objective of this study is determination of environmental remediation cost (EE_{ENV}) of industrial solid waste in terms of "Extended Exergy". Extended Exergy Accounting (EEA) is an exergoeconomic methodology which proposes a computation technique to determine the resource consumption equivalent of immaterial/nonenergetic production factors (labor, capital, and environmental remediation costs) in terms of a unified metric: exergy. Since all the material, energetic and immaterial/nonenergetic factors are taken into account, EEA provides more reasonable and directive results on "resource consumption" side of the issue. EE_{ENV} is represented by the cumulative exergetic consumption of resources to attain an ideal, zero-impact disposal of the effluent. This is the first study in the literature that EE_{ENV} of industrial solid waste is obtained in accordance with the original methodology of EEA. The waste treatment system consists of material recycling, incineration, anaerobic digestion and landfilling. The waste treatment procedure is applied to Turkish industrial waste composition.

Keywords: Extended exergy accounting, EEA, Industrial waste, Ecological accounting, Environmental remediation cost

Introduction

In the last decades, scientists, researchers and engineers paid a great attention to the concept of exergy and routinely applied exergy analysis to various industrial processes. "Exergy" (available energy) is defined as the maximal amount of work that can be extracted from the system in the process of reaching equilibrium with the environment (dead state) (Szargut, Morris, & Steward, 1988). This definition underlines the impossibility of obtaining further work from a system which is in equilibrium with the dead state. Hence, exergy can be regarded as the part of the physical resource used (consumed) in all types of anthropic activities and serves as a rationally unified measure of utility and scarcity. The exergy content of a natural resource characterizes "the measure for potential usefulness" (in other words, quality), i.e., its ability to perform "useful work" (Ayres & Ayres, 1999). The main advantage of an exergy based analysis compared with the more traditional energy analysis is the identification and quantitative assessment of global and local irreversibilities, which result in a measure of resource degradation in the processes. Besides, the exergy concept provides a unified quantifier which can be used in the evaluation of resource quality (material or immaterial). Exergy is not a direct measure of pollution (Sciubba, 2009) but indicates the potential to cause change in the environment since it is also a measure of distance between a released substance and the environmentally neutral (pseudo-equilibrium) state. It ought to be noticed that exergy does not directly measure, for instance, toxicity (Sciubba, 2009; Zhang & Chen, 2010).

Extended Exergy Accounting (EEA) is an exergy based resource use analysis methodology in which material and/or immaterial commodities are represented by extended exergy (EE) which is equal to exergy of resources consumed to generate them (Sciubba, 2001, 2003a). EEA proposes a novel calculation procedure to express the resource equivalent of externalities (labour, capital and environmental impact) in terms of exergy, and externalities are accounted for in the EE of a commodity. In other words, summation of the resource equivalent of "materials, energy carriers, capital and labour consumed during the production of the commodity and environmental remediation cost (EE_{ENV})" is named extended exergy (EE) of a commodity (Sciubba, 2003a, 2005). In EEA theory, all consumed materials, energy carriers and also immaterial/nonenergetic production fluxes (capital, labour, and environmental damage) are represented in terms of exergy and provides a good measure of resource which are irreversibly consumed in the life cycle of a material or immaterial commodity. Thus, the global problem of resource depletion and environment damage can be monitored by EEA, which is in essence a carefully and rigorously defined extension not of the concept of exergy but of its application to measure different fluxes (Sciubba, 2003a, 2003b, 2011). Once the numeraire of extended exergy (which is a strictly thermodynamic quantity that expresses the amount of equivalent exergy "embodied" in a commodity) is employed as the sole measure of resource consumption, it is automatically followed with minimization of exergy use and destruction which are essential for improving the degree of sustainability. Hence, EEA offers more insight than other exergy based methods in the literature (Sciubba, Bastianoni, & Tiezzi, 2008).

The present paper focuses on the determination of "environmental remediation cost (EE_{ENV})" of solid waste originated by Turkish industrial sector in the year 2010. In theoretical structure of EEA methodology, the concept of "environmental remediation cost" relies on the "zero impact" approach which can be described as: bringing the state of effluent streams to the state of thermodynamic equilibrium with the reference state before being discharged into the environment (*i.e.*, the discharged effluent has "zero impact" on the environment) (Sciubba, 2003b). The essence of this idea is representing the environmental impact of the effluent by the cumulative amount of resources (in terms of exergy) that must be consumed or employed to attain an ideal, zero-impact disposal of the effluent. The cumulative amount of consumed resources is called "environmental remediation cost (EE_{ENV})" in EEA methodology. In brief, EE_{ENV}, which represents the environmental impact of the effluent, is not proportional to the physical exergy of the effluent, but it is equal to the extended exergy (sum of the material exergy and physical exergy, plus exergetic equivalent of externalities -labour and capital required for the installation and operation of the process and also environmental remediation cost of possible effluents from treatment process which must be cleaned) ideally required to cool the effluent to T_0 and break it up into its constituents such that each one of them is in equilibrium conditions with the surroundings (Sciubba, 2005). To date, in the literature, EE_{ENV} is calculated via conversion of monetary expenses of the considered remediation system into its extended exergy equivalent (Chen & Chen, 2009; Ptasinski, Koymans, & Verspagen, 2006; Sciubba, Bastianoni, & Tiezzi, 2008). In this study, EE_{ENV} of solid waste is obtained in accordance with the original calculation procedure of EEA (a real treatment procedure is analyzed). The analyzed "environmental remediation system" for solid waste consists of material recycling, incineration, anaerobic digestion (biogas production) and landfilling. The approach is applied to the case of industrial solid waste generated in Turkey in the year 2010.

EEA Method and the Waste Treatment System

In Equation 1, EE (extended exergy) of a commodity is seen (Sciubba, 2003a):

$$EE = E_M + E_{phys} + EE_L + EE_C + EE_{ENV} \tag{1}$$

where E_M and E_{phys} are exergy of materials and energy carriers, respectively; EE_L and EE_C are total exergetic equivalent of labour and capital, respectively; EE_{ENV} is the exergetic equivalent of environmental remediation cost. Computation of exergetic equivalent of labour and capital is presented in Section 4. Equation for EE_{ENV} is presented in (2):

$$EE_{ENV} = E_{M\text{-}t} + E_{phys\text{-}t} + EE_{L\text{-}t} + EE_{C\text{-}t} + EE_{Env\text{-}t} - E_{P\text{-}t} \tag{2}$$

where E_{M-t} and E_{phys-t} are respectively the exergy of material and energy carriers received by the environmental remediation system; EE_{L-t} and EE_{C-t} are respectively the exergetic equivalent of labour and capital received by the environmental remediation system, E_{P-t} is the exergy of the treatment system "possible" product P_t. System flows are illustrated in Fig. 1. In Fig.1, E_W is the exergy of the system effluent (in this case, effluent is "solid waste") and not seen in above equations (1) and (2), since E_W is an internal flow between "system" and "environmental remediation system" which are regarded as a combined system in EEA analysis.

The definition of environmental remediation cost is presented in Section 1. Since, in reality, there is no totally "clean" technology (Sciubba, 2003b) or present treatment technologies don't always produce effluents in equilibrium with the surroundings, choosing the minimum environmentally hazardous technology, i.e., "consciously accepted" level of pollution, is a reasonable approach (Sciubba, 2002) and applied in this study.

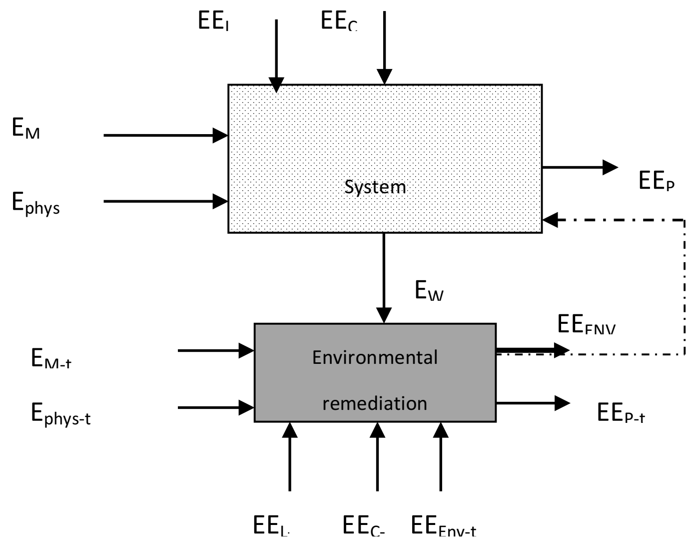

Figure 1. A commodity-producing process with flows considered in EEA methodology

Recycling of industrial waste can be classified into two parts: 1) heat & energy generation by using the combustible part as a fuel; 2) recycling and reusing of the recyclable part.

Most of the combustible components in industrial solid waste are also biodegradable, thus, a combustible gas can be obtained from a biological conversion process (UNEP, 2005). The AD process can be briefly described as: a biological process during which the complex organic matter is decomposed by anaerobic microorganisms in the absence of oxygen (*i.e.*, under anaerobic conditions). The products are primarily methane (CH_4) with an accompanying production of other gases (mainly CO_2) (United Nations Environment Programme, 2005). Anaerobic digestion reduces the quantity of organic waste ending up in landfills and also methane emissions from landfill areas. Among the other methods, anaerobic digestion (AD) has very special importance due to its ability of biogas generation (which is composed of 60–70 vol.% of methane, CH4) and providing the option of energy generation via biogas utilization (Appels *et al.*, 2008). This energy gain by biogas utilization provides cost effectiveness and minimizing the mass and volume of final sludge disposal (Tchobanoglous, Burton, & Stensel, 2002). Another advantage of AD process is: the residue (digestate) can be composted further to produce "compost" (a kind of fertilizer) which is another product of AD process (MREC, 2003; EEA, 2002; Poschl, Ward, & Owende, 2010). The digestate contains compounds of agricultural value: it is rich in nitrates and performs well as fertilizer (Corrado, Fiorini, & Sciubba, 2006). As a result, due to its cost effectiveness and reduced environmental impact, AD is considered as a major and essential part of modern wastewater treatment plants (Appels *et al.*, 2008).

To sort and process the waste, 2 types of facilities have common use: MRF (Materials Reprocessing Facility) and MBT (Mechanical Biological Treatment). Both of them comprise sorting of waste but in MRF, following procedure after sorting consists of recycling and/or fuel manufacturing (made of waste) and/or preparing the constituents of waste as raw material of different industrial processes (Smith *et al.*, 2001). In MBT, the following procedure includes biological treatment of waste constituents (organic part) such as Anaerobic Digestion (AD) or composting (GCC, 2010). Applied treatment procedure to industrial sector solid waste in this study can be described as: collected waste is transferred to MRF where the waste is split into its components (organic part is separated from inorganic part as well as the inorganic part is sorted into constituents) and inorganic part is pre-treated and recycled. The organic fraction is mostly made of kitchen garbage while mainly plastics, paper & cardboard, wood, textiles and rubber constitute the inorganic fraction. Non-recyclable part of considered inorganic materials are transferred to an incineration plant where electricity and heat are produced by CHP (combined heat and power system). Remaining materials of recycling process in MRF (sent to recycling but not recycled) and ash produced from incineration of non-recyclables (in incineration plant) are landfilled (see Fig 2). The only discharge to the environment is this landfilled part which has no greenhouse gas emission capacity to the atmosphere after landfilling (Chen & Cheng, 2008).

The organic fraction is transferred from MRF plant to another plant and undergoes AD process in order to produce biogas (CH_4+CO_2). Afterwards, biogas is upgraded by removing CO2, H2S *etc.* and resulting gas (98% of CH4 by vol.) is used as a substitute for natural gas. The digestate, *i.e.*, the residue of the anaerobic digestion, is composted and produced compost is taken out of the system as a system product.

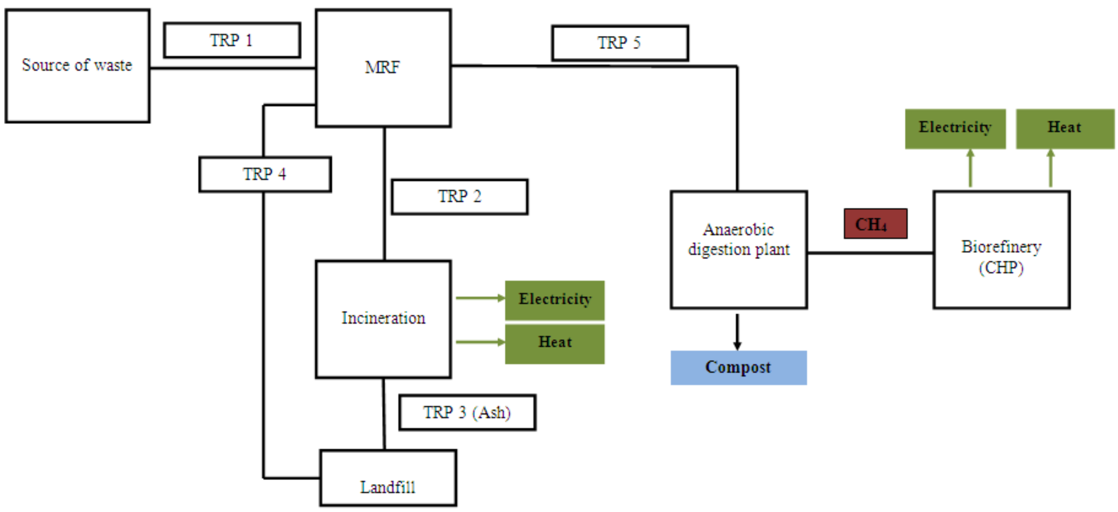

Figure 2. Illustration of household sector solid waste treatment system

EEA analysis of the industrial solid waste treatment system

The approach is applied to the case of solid waste generated in Turkish industrial sector in the year 2010. The composition of IN sector solid waste is presented in Table 1. The composition is estimated based on data (SWAP, 2005) due to the fact that there is neither official data nor study in the literature for average composition of Turkish IN sector waste. Unfortunately, in Turkey, hazardous waste is mostly landfilled and very limited amount is recycled and reused. Uncontrolled production of hazardous waste and illegal dumping or discharging to receiving water bodies are one of the primary problems arising along with industrial activities in Turkey (Salihoglu, 2010). As a result, treatment of hazardous waste is a very important issue for the country, but, since it takes special technologies and detailed analyses, it is taken out of the scope of this thesis. In other words, since the hazardous waste has a little share in the total composition of IN sector solid waste, environmental remediation cost of relevant part is neglected.

In EEA methodology, IN sector covers all manufacturing industry including construction. Mining & quarrying activities, energy generation and fuel production processes (heat and electricity generation, all refinery activities, coal processing activities) are covered by other sectors.

Table 1. Composition of IN sector waste (based on data in Switzerland Global Enterprise, 2015; Turkstat, 2011).

Composition	Percent (% wt.)	Amount (Ton)
Organic	18.21	2490945.9
Paper&Cupboard	32.38	4429260.2
Textile	2.19	299570.1
Plastic	20.06	2744007.4
Glass	0.55	75234.5
Metal (Al)	0.23	31461.7
Metal (Fe)	10.31	1410304.9
Other metals (Cu)	0.12	16414.8
Wood	3.61	493811.9
Other combustibles	4.38	599140.2
Ash	3.97	543056.3
Hazardous waste	3.99	545792.1
Total	100	13679000

Summarizing tables of EEA analysis for industrial sector solid waste treatment system which report the results of the material, energy carrier, capital and labour inflows into the sector, are seen between Table 2- 6.

The necessary truck numbers for each transportation line and exergetic content of the trucks are presented in Table 2 (exergy of one truck is computed as 0.045 TJ/truck in a different study of the author (Seckin, Sciubba, & Bayulken, 2013) and is inserted into the computation here). In Table 2, TRP lines signify the transportation lines seen in Fig. 2. In calculation of material influxes (except trucks), since no sufficiently reliable data were available on the exact material composition of the used items in the system, and thus an analytical analysis was impossible, the corresponding portion of EE_{ENV} is computed by converting the known monetary cost of the process into exergetic equivalent by means of ee_K (J/$). Computation and numerical value of ee_K is presented in Section 4. The exergy of material flow pertaining to other systems or processes except TRP lines are computed as explained above and presented in Table 3. (Exchange rate between $, € and TL: 1,8 TL= 1 €= 1,26 $ for 2010).

Table 2. Number of trucks and their exergetic content

Transportation line	Number of trucks	Exergy (TJ)
TRP-1	2415	108.68
TRP-2	26	1.17
TRP-3	14	0.63
TRP-4	48	2.16
TRP-5	115	5.18
Total	2617	117.77

Table 3. Material exergy (E_{M-t}) of systems and processes except transportation lines

System/Process	Capital	Ref.	Equivalent exergy (TJ)
MRF plant	100 €/Ton	Smith *et al.*, 2001	30527.47
Incineration plant	64 €/Ton	Smith *et al.,* 2001	4515.57
Anaerobic digestion plant	65 €/Ton	Smith *et* al., 2001	5201.14
Upgrading of biogas	0,26 €/m^3	De Hullu *et al.*, 2008	2727.18
Biorefinery	7000 $/$KW_{el}$	EIA, 2012	13429.19
Seperation, composting	35 €/Ton	Smith et al., 2001	1120.25
Total			57520.80

[1] *The cost of MRF plant includes preliminary sorting, pre-treatment of recyclable materials and recycling*

[2] *Anaerobic digestion plant includes mixing, sterilization and anaerobic digestion part*

In conclusion, exergy of material transfers (E_{M-t}) into the system is the sum of Table 2 and Table 3 which is 57638.56 TJ.

The only exergy inflow of energy carriers (physical exergy) are the diesel fuel consumption of transportation lines. Calculation of diesel fuel consumption for each line is computed based on data presented in (Berglund & Borjesson, 2006) and the results are presented in Table 4. (Exergy of diesel fuel is 46366,71 MJ/Ton).

Table 4. Physical exergy (E_{phys-t}) inflow of the environmental remediation system

	Diesel Consumption (Ton)	Exergy of diesel consumption (TJ)
TRP-1	315726.39	14639.20
TRP-2	2771.12	128.49
TRP-3	1385.56	64.24
TRP-4	4826.98	223.81
TRP-5	10475.78	485.73
Total		15541.47

In capital flows, capital investment of the system (Investment cost, IC) is assumed to be supplied by bank credit with annual interest rate of 20% and payback time of 10 years. Annual payment is calculated using the methodology presented by (Bejan, Tsatsaronis, & Moran, 1996) (annual payment is 23.85% of capital investment, calculation is presented in (3) and (4)). Annual "fixed and varying operation costs" (including insurance, wages, maintenance etc., totally abbreviated as "OP") are assumed to be 20% of capital investment. Capital flow of the system is sum of "annualized investment cost plus OP" of each process and system, results are seen in Table 5-7.

$$\text{Annualized cost} = \text{Present value}(IC) \times \left[\frac{r}{1 - \left(\frac{1}{(1+r)^n} \right)} \right] \tag{3}$$

where r is the annual interest and n is the number of pay back years.

$$\text{Annualized cost} = \text{Present value}(IC) \times \left[\frac{0.2}{1 - \left(\frac{1}{(1+0.2)^{10}} \right)} \right] = 0.239 \tag{4}$$

Table 5. Exergetic equivalent of the capital of processes

System/Process	Capital	Exergetic equivalent of IC (TJ)	Exergetic equivalent of annualized IC (TJ)	Exergetic equivalent of OP (TJ)	Annualized IC+OP (TJ)
MRF plant[1]	100 €/Ton	30527.47	7296.07	6105.49	13401.56
Incineration plant	64 €/Ton	4515.57	1079.22	903.11	1982.33
Anaerobic digestion plant[2]	65 €/Ton	5201.14	1243.07	1040.23	2283.30
Upgrading of biogas	0,26€/m^3	2727.18	651.80	545.44	1197.23
Biorefinery	7000 $/$KW_{el}$	13429.19	3209.58	2685.84	5895.42
Separation, composting	35 €/Ton	1120.25	267.74	224.05	491.79
Landfilling	10 €/Ton	586.06	140.07	117.21	257.28
Total					25508.91

[1] *The cost of MRF plant includes preliminary sorting, pre-treatment of recyclable materials and recycling*
[2] *Anaerobic digestion plant includes mixing, sterilization and anaerobic digestion part*

Use of trucks with an accompanying consumption of diesel fuel brings about capital inputs into the system. The number of trucks and diesel fuel consumption in each TRP line are presented in Table 6 and Table 7, respectively. It is assumed that investment cost of 1 truck is 100000 TL (69930,07 $) as well as annual operation and maintenance cost (OP) is 20% of the investment cost. Density of diesel fuel is taken as 0.835 kg/lt and for the year 2010, the price of diesel fuel is 2.1 TL/l (1.47 $/l) (BP, 2016). Diesel fuel cost is accounted in OP cost. As a result, its capital equivalent is not annualized in calculations.

Table 6. Exergetic equivalent of the capital of trucks

Transportation line	Number of trucks	Exergetic equivalent of IC (TJ)	Exergetic equivalent of annualized IC (TJ)	Exergetic equivalent of OP (TJ)	Annualized IC+OP (TJ)
TRP-1	2415	4306.55	1027.21	861.31	1888.53
TRP-2	26	46.36	11.06	9.27	20.33
TRP-3	14	24.97	5.95	4.99	10.94
TRP-4	48	85.60	20.42	17.12	37.54
TRP-5	115	205.07	48.91	41.01	89.93
Total	2617				2047.27

Table 7. Exergetic equivalent of the capital of diesel fuel consumption

Transportation line	Diesel Consumption (l)	Exergetic equivalent of diesel cost (TJ)
TRP-1	378115434.25	14173.66
TRP-2	3318705.07	124.40
TRP-3	1659347.82	62.20
TRP-4	5780810.42	216.69
TRP-5	12545838.76	470.28
Total		15047.23

Due to the lack of data on landfilling, material input coming from landfilling process (tractors, excavators, etc.), energy consumption with accompanying emissions are disregarded in this study. In conclusion, sum of capital fluxes is the sum of Table 5, 6 and 7 which amounts to 42603.41 TJ.

In the matter of the labour consumption of the system, labour consumed by TRP lines are calculated based on driven distance and average speed of the trucks which are assumed based on (Berglund & Borjesson, 2006). For the left of the system, it is assumed that labour of a CHP system is 200 workers per 1000 MW_{h+el} generated energy, based on data in (Bezdek & Wendling, 2010). Considering the whole system, number of workers is assumed to be 400 workers per 1000 MW_{h+el} with 1800 workhours/year workload for each worker.

Generated electricity and heat power is presented later in Table 14 as 20701.61 TJ_{el} and 24841.92 TJ_{h}. Generated power is computed as:

$$\text{Generated power}\,(MW_{el+h}) = \frac{\text{Generated energy}\,(MJ_{el+h})}{\text{Annual working time (s)}} = \frac{(20701.61 + 24841.92)\,x\,10^{6}}{340x24x60x60} = 1550.36 \tag{5}$$

Hence, labour consumed in the system (excluding transportation) is:

$$\text{Labour (workhours/year)} = \left[\frac{400\,\text{workers}}{1000\,\text{MW}}\right] x \left[\text{Annual work hours}\right] x \left[\text{Generated power}\,(MW_{el+h})\right] \tag{6}$$

$$\text{Labour (workhours)} = \left[\frac{400\,(\text{workers})}{1000\,(\text{MW})}\right] \text{x} \left[1800\,(\text{hours / year worker})\right] \text{x} \left[1550.36\,(\text{MW})\right] \tag{7}$$

$$\text{Labour} = 1116263.21 \text{ hours}$$

The exergetic equivalent of the labour is computed by means of ee_L:

$$EE_L = \text{Labour load (workhours) x } ee_L \text{ (MJ/hours)} = 1116263.21 \text{ x } 153.95 = 171848720.92 \text{ MJ} = 171.84 \text{ TJ} \tag{8}$$

Resulting labour consumption and exergetic equivalent are presented in Table 8.

Table 8. Labour consumption and exergetic equivalent (EE_L)

Transportation line	**Labour (workhours)**	**Exergetic equivalent of labour (TJ)**
TRP-1	7731483.28	1190.28
TRP-2	70673.37	10.88
TRP-3	36407.49	5.61
TRP-4	120465.96	18.54
TRP-5	260563.42	40.12
The left of the system		171.84
Total		1437.27

Environmental remediation cost of the system (EE_{ENV-t}) stems mainly from transportation as well as processes like anaerobic digestion, incineration etc. The emission gasses are obtained based on (Eggleston *et al.*, 2006) and presented in Table 9. Due to lack of sufficiently disaggregated data and great variety of emission gasses, three types of greenhouse gasses (CO_2, CH_4, N_2O) are considered in this study.

Table 9. Greenhouse gas emissions from the processes

	Emission (Ton)		
	CO_2	N_2O	CH_4
TRP-1	1001109.37	52.69	52.69
TRP-2	8786.70	0.46	0.46
TRP-3	4393.34	0.23	0.23
TRP-4	15305.44	0.81	0.81
TRP-5	33216.72	1.75	1.75
Incineration plant	2780827.81	121.30	909.76
Anaerobic digestion	8850.87		3515.22
Upgrading of biogas	279559.22		2273.18
Biorefinery	309955.22	0.55	5.53
Composting	131492.19	298.84	3984.61
Total	4573496.87	476.63	10744.24

The environmental remediation cost (EE_{ENV}) of considered emission gases are computed in a different study of the same author (Seckin, Sciubba, & Bayulken, 2013). But, since the goal of the present study is determining the environmental remediation cost for solid waste, presenting the computation for gas treatment would be deviation from the subject. Hence, EE_{ENV} of considered gases are inserted into Table 10 to obtain the $EE_{ENV\text{-}t}$ for the whole solid waste treatment system.

Table 10. Environmental remediation cost of emission gasses (EE_{ENV})

CO_2 emissions (Ton)	4573496.87
N_2O emission (Ton)	476.63
CH_4 emission (Ton)	10744.24
CO_2 $ee_{ENV\text{-}g}$ (TJ/Ton CO_2)	0.043
N_2O $ee_{ENV\text{-}g}$ (TJ/Ton N_2O)	0.01
CH_4 $ee_{ENV\text{-}g}$ (TJ/Ton CH_4)	0.267
CO_2 $EE_{ENV\text{-}g}$ (TJ)	196660.37
N_2O $EE_{ENV\text{-}g}$ (TJ)	4.77
CH_4 $EE_{ENV\text{-}g}$ (TJ)	2868.71
Total $EE_{ENV\text{-}t}$ (TJ)	199533.84

As it is seen in Fig.2, the products of the whole treatment system are 1) electricity and heat produced by incineration of non-recyclable part of the inorganic waste and 2) electricity and heat produced in biorefinery 3) recycled materials and 4) compost. The ash generated in considered processes are assumed to have zero exergy. Hence, its exergetic content is not included in exergy of products. The amount of non-recyclables and their energy content are presented in Table 11. The amount of the materials in Table 11 is derived based on data in (Rigamonti, Grosso, & Giugliano, 2009).

Table 11. Low heating value (LHV) of the non- recyclables

	Material (Ton)	LHV (MJ/kg)	Total energy content (TJ)
Paper & Cupboard	642242.73	11.50	7385.79
Textile	121325.89	14.60	1771.36
Plastic	1134921.46	31.50	35750.03
Glass	4514.07	0.00	0.00
Metal (Al)	3665.29	0.00	0.00
Metal (Fe)	349755.61	0.00	0.00
Other metals (Cu)	1641.49	0.00	0.00
Wood	71602.72	18.46	1321.79
Total	2329669.26		46228.96

Efficiencies of heat and electricity production and produced energy via incineration are seen in Table 12.

Table 12. Properties of incineration process

		Electricity	Heat
Energy of non-recyclables (TJ)	46228.96		
Efficiencies		0.40	0.48
Produced energy (TJ)		18491.58	22189.90

The composition of biogas utilized in the biorefinery involved in the system is 98% CH_4 and 2% CO_2. The biorefinery is a CHP plant and the efficiencies of heat and electricity generation are assumed to be same as those in Table 12. The amount of the biogas utilized in biorefinery and produced energy can be seen in Table 13. LHV (low heating value) of CO_2 is almost zero (De Hullu *et al.*, 2008).

Table 13. Properties of biogas utilization

CH4 (m3)	163839264.48
CO2 (m3)	3343658.46
LHV of CH4 (MJ/m3)	33.73
LHV of CO2 (MJ/m3)	0.00
LHV of biogas (TJ)	5526.30
Electricity generation efficiency	0.40
Heat generation efficiency	0.48
Generated electricity (TJ)	2210.52
Generated heat (TJ)	2652.62

As stated earlier, the energy need (both of heat and electricity) is met by the generated energy in the system, i.e., output of biorefinery and incineration process. The energy balance of the environmental treatment system is presented in Table 14. In the Table, it is assumed that produced heat is at the temperature of 100 C.

Table 14. Energy balance of the system

Description		Consumption		Production	
		Electricity (TJ)	Heat (TJ)	Electricity (TJ)	Heat (TJ)
MRF plant	preliminary sorting	196.07			
MRF plant	pretreatment of recyclable materials and recycling	4129.53	6726.68		
Incineration plant		832.12		18491.58	22189.90
Anaerobic digestion	mixing, sterilization	538.05			
Anaerobic digestion	anaerobic digestion	88.42	663.15		
Upgrading of biogas		359.10	117.52		
Biorefinery		99.45		2210.03	2652.02
Composting	Separation, drying, composting	586.47			
Total		6829.21	7507.35	20701.61	24841.92
Net production				13872.41	17334.57
Exergy of production				13872.41	3484.10

Recycling of the materials is analyzed in accordance with technical details of recycling processes given in (Rigamonti, Grosso, & Giugliano, 2009). Amount of recycled materials and exergy contents are reported in Table 15. Produced compost from residue of the AD process (digestate) is presented in Table 16.

Table 15. Amount and exergy of recycled materials

	Recycled material (Ton)	Specific exergy (MJ/Ton)	Exergy (TJ)
Paper& cardboard	3787017.47	17000	64379.297
Textile	178244.21	13904.76	2478.44292
Plastic	1609085.94	32502.16	52298.7687
Glass	70720.43	131.48	9.2983224
Metal (Al)	27796.41	32928.09	915.282752
Metal (Fe)	1060549.29	6740.69	7148.83399
Other metals (Cu)	14773.31	2112.06	31.202125
Wood	422209.18	20658.24	8722.09851
Total			135983.224

Table 16. Amount and exergy of produced compost

Amount of produced compost (Ton)	398461.19
Exergy of compost (MJ/Ton)	18373.31
Exergy of total produced compost (TJ)	7321.05

Calculation of exergy equivalent of externalities

The exergetic equivalent of labor (ee_L) is defined as the exergy used to generate one work-hour and calculated as (9):

$$ee_L = \frac{\alpha \text{ x } E_{in}}{N_{wh}} \quad (9)$$

where, ee_L(MJ/hour), exergetic equivalent of labor; ✓, the fraction of the primary exergy embodied into labour; E_{in} (MJ/year), global exergy influx and N_{wh} (hours/year), cumulative number of work hours (Sciubba, 2011).

The unit exergetic equivalent of capital (ee_K) is defined as the equivalent primary exergy resource embodied in one monetary unit and calculated as (10):

$$ee_K = \frac{\alpha \times \beta \times E_{in}}{(M_2 - S)} \quad (10)$$

where, ee_K (MJ/\$), exergetic equivalent of capital; β, an amplification factor that accounts for the creation of wealth due to exclusively financial activities (TalensPeiró, 2010); M_2 (\$/year), money + quasi-money circulation; S (\$/year), global wages and salaries in a country.

Exergetic equivalent of labour and capital is calculated as:

$$EE_L = L \text{ x } ee_L \quad (11)$$

$$EE_C = C \text{ x } ee_K \quad (12)$$

where, L(hours), workhours; C(\$), capital; EE_L and EE_C are defined in Section 1.

To calculate the econometric factors ✓and 🚲 (13-16) are occupied:

$$E_{used} = 365 \text{ x } f \text{ x } e_{surv} \text{ x } N_h \quad (13)$$

$$f = \frac{HDI}{HDI_0} \tag{14}$$

$$\alpha = \frac{E_{used}}{E_{in}} \tag{15}$$

$$\beta = \frac{M_2 - S}{S} \tag{16}$$

where, E_{used} (MJ/year), the global exergy used by the society for survival, e_{surv} ($1{,}05x10^7$ J/(person·day)), exergy consumption for survival; N_h (persons), number of inhabitants; HDI, Human Development Index; HDI_0, Human Development Index of a primitive society, 0.055 (TalensPeiró, 2010). A further discussion is available in (Sciubba, 2011). Data for M_2, S, N_h, HDI are obtained from (Turkstat, 2009; Turkstat, 2010;TMIA, 2010; UNDP, 2010), respectively. Above listed variables and ee_L and ee_K for Turkey are seen in Table 17.

Table 17. Econometric factors, ee_L and ee_K

E_{in} (TJ)	3601655961.68
HDI	0.798
M_2 ($)	208206113706
S ($)	170782627832
N_{wh}	28266496268.07
N_h	78259264
✔	0.001208
🚲	0.219
ee_L (MJ/hours)	153.952
ee_K (MJ/$)	25.5

Results

The formulation of EE_{ENV} is presented in (1). Products of the analyzed remediation system (E_{P-t}) are seen in Table 18. The terms which are seen in (1) (E_{M-t}, E_{phys-t}, EE_{L-t}, EE_{C-t}, EE_{ENV-t}) and resulting EE_{ENV} for IN sector solid waste are presented in Table 19.

Table 18. Products of the remediation system

Products	Exergy (TJ)
Electricity	13872.41
Heat	3484.10
Recycled materials	135983.22
Compost	7321.05
Total (E_{P-t})	160660.78

Table 19. EEENV for IN sector solid waste

	Exergetic equivalent (TJ)
E_{M-t}	57638.57
E_{PHYS-t}	15541.47
EE_{L-t}	1437.27
EE_{C-t}	42603.41
EE_{ENV-t}	199533.84
E_{P-t}	160660.78
EE_{ENV-s}	156093.78

Conclusion

In this study, EE_{ENV} of solid waste is obtained in accordance with the original calculation procedure of EEA. Analysed "environmental remediation system" consists of material recycling, incineration, anaerobic digestion (biogas production) and landfilling. This is also a case study which analyses the extended exergetic cost of sectoral solid waste treatment for industrial sector of Turkey for the year 2010. It is noteworthy that, in this study, solid waste environmental remediation cost (EE_{ENV}) is computed for a selected disposal process chain in which state-of-the-art industrial treatment systems are incorporated. In above sections of this paper, it is seen that composition of solid waste and type of waste treatment processes directly dominate the quantity of EE_{ENV}. Hence, different effluent remediation technologies must be analysed and corresponding EE_{ENV} values should be determined. Thereby, the authorities can see and choose the minimum resource consuming waste handling and treatment routes for more sustainable applications. This study presents numerical results for state-of-the-art industrial treatment technologies and has the corresponding importance. Hence, the most important consequence of the present study is the necessity of further examination of different handling and treatment routes to determine the lowest extended exergetic cost of EE_{ENV} for industrial solid waste.

As it is seen in Table 19, EE_{ENV} of considered industial waste composition is 156093.78 TJ. Total amount of considered waste is 13679000 Ton (Table 1). As a result, specific environmental remediation cost of industrial solid waste (ee_{ENV}, per unit mass EE_{ENV}) is computed as:

$$ee_{ENV} = \frac{EE_{ENV}}{\text{Solid waste}} = \frac{156093.78\ \text{TJ}}{13679000\ \text{Ton}} = 0.0114\ \text{TJ/Ton} \quad (17)$$

Similar analyses are performed for municipal solid waste and tertiary sector solid waste in earlier studies for the year 2006 (Seckin & Bayulken, 2012a, 2012b). Results are 0.0216 TJ/ton-waste and 0.023 TJ/ton-waste for tertiary sector and municipal solid waste, respectively. ee_{ENV} determined for industrial solid waste in this study is relatively lower due to the different waste composition of the sector. It is concluded that low organic waste and relatively higher recyclable portion (primarily paper & cupboard and plastics) in total waste content results in higher recycled materials in system products (as presented in Table 18), hence, lower EE_{ENV} (based on (1)) and lower specific environmental remediation cost for industrial solid waste.

Nomenclature

AD	anaerobic digestion
CExC	cumulative exergy consumption, J
CHP	combined heat and power
E	exergy, J
EE	extended exergy, J
ee	specific extended exergy, J/(hour, mass, $,...)
EEA	extended exergy accounting
EE_{ENV}	environmental remediation cost, J
E_{in}	global exergy influx, J/year
E_{used}	the global exergy used by the society for survival (J/year)
HDI	human development index
IC	investment cost, $
LHV	low heating value, J
M_2	money + quasi-money circulation, $/year
N_h	population
N_{wh}	cumulative number of work hours, hours
OP	operation and maintenance cost, $
P	product
S	global wages and salaries in a country, $/year
T_0	ambient temperature, °C
TRP	transportation line

Greek symbols

$	Dollar
€	Euro
🚲	an amplification factor represents the creation of wealth due to exclusively financial activities
✔	fraction of the primary exergy embodied into labour

Subscripts and superscripts

C	capital
el	electrical
ENV	environmental remediation
h	heat
L	labour
M	material
phys	physical
t	for treatment system

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4

Maximizing Overall Energy Performance of a Multiple Use Building by Integrating Advanced Building System

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Abstract

According to recent studies, building consumption covers nearly 30-40% of total energy consumption in developed countries. Considering this in the city scale, building energy efficiency has become more significant in the case of energy consumption and carbon footprint reduction. In this study, a set of renovation intervention's strategies were investigated in a multiple used building as a case study. The renovation strategies were based on detailed existing building energy performance analysis which has 18.108 m^2 conditioned area with a multifunctional use including a restaurant, gymnasium, doctor rooms, terraces and 228 residential rooms for elderly accommodation. The existing building's systems have conventional type of heating and cooling systems; air cooled chiller for cooling, and natural gas boilers for heating and DHW needs. In the study, existing case conditions were improved by proposed interventions which are integration of insulation and replacement of lighting systems and windows. Also major renovation has done to improve the mechanical systems by integrating renewable systems such as solar thermal and heat pump systems as well as monitoring and controlling systems. The detailed energy performance analysis of the building and systems were introduced in this paper. As a result of the proposed interventions and advanced building system integration, more than 60% improvement in energy and correspondingly a 70 kg/m^2year approximate greenhouse gas emission reduction were estimated throughout whole year period in the building.

Keywords: Energy Efficiency, Energy Efficient Building Design, Sustainability, Zero Energy Buildings

Introduction

Development in the technology and industry fields has led the energy consumption increase in the recent years. Since the global need for energy has been increasing with each passing day, its environmental effects and energy consumption have become greater unavoidably. According to International Energy Agency statistics, CO_2 emissions from fuel combustion has increased by 130% from 1971 to 2013 (IEA, 2015). Furthermore, researches reveal that buildings are responsible for nearly 40% of the total energy consumption in developed countries (UNEP, 2009; Perez-Lombard et al., 2008). Considering this in the city scale, building energy efficiency has become more significant in the case of energy consumption and carbon footprint reduction. Accordingly, energy efficiency in buildings is regarded as one of the most critical and significant topics in the field of energy. The main aim is to investigate how to maximize energy savings and reach better efficiencies by utilizing renewable energy sources for building's energy needs (Aksamija, 2016). In the literature, a variety of researches can be found referring to optimization of building energy consumption. Rose and Thomsen have investigated energy saving potential of non-residential buildings in Denmark by applying a wide range of energy efficiency measures ranging from the application of renewable systems to optimization of building envelope (Rose and Thomsen, 2015). Retrofitting activities are resulted with 45 to 85% less energy consumption amongst four exemplary project. Using a similar approach but referring residential buildings this time, Wang and Holmberg weighed the energy saving potential of four retrofitted Swedish buildings. Within the retrofitting activities, energy reduction was found out to be 36 to 54% (Wang & Holmberg, 2015). Additionally, Lam, Wang and Yang investigated the consumption profile of 10 office-buildings in China. (Lam, Wang & Yang, 2008) According to the consumption profiles of the buildings; a variety of Energy Conservation Measures (ECMs) are identified. Using a parametric and sensitivity analysis by dynamic building simulation techniques, it is found out that up to 14% electricity savings is possible. In another research by Causone et al., zero energy building concept is addressed in a residential building (Causone et. al., 2014). To obtain the maximum energy performance, high thermal performance building envelope materials have been used as well as application of renewable technologies and passive strategies such as free cooling or natural ventilation in a pilot single family house. The building's performance is obtained monthly via energy simulation. Results have revealed that a big portion of the energy consumption can be covered by applying convenient technologies and control strategies and accordingly energy efficiency can be increased. Similar approach have been conducted in Alajmi et al.'s study, yet, in a hot climate. (Alajmi, et.al., 2016) Using the renewable technologies, nearly zero energy building target is obtained in a building placed in Kuwait. The study has resulted with lower consumption ratios and up to 848 tons of CO_2 reduction. Also in economic aspect, a considerable number of researches have proved that when appropriate technologies are applied considering a number of parameters such as building type, climatic conditions or occupant profiles, building are improved not only on the basis of energy and environmental issues but also economically in long term. (Zavadskas et.al, 2016; Goggins et. al; 2016; Ferrara et. al., 2016)

The objective of this study is to investigate and maximize the overall performance of a multiple-use building by integrating different interventions and strategies. In the paper, a set of renovation intervention's strategies are investigated in a multiple used building as a case study. The selected building, which is represented in Figure 1, is located in Istanbul at Yakacik district of Kartal.

Figure 1. Demo building (Kartal Elderly House)

The building was built as an elderly house and has 8 stories. The renovation strategies are based on detailed existing building energy performance analysis which has 18.108 m2 conditioned area with a multifunctional use including a restaurant, gymnasium, doctor rooms, terraces and 228 residential rooms for elderly accommodation. The existing building's systems have conventional type of heating and cooling systems; air cooled chiller for cooling, and natural gas boilers for heating and DHW needs.

Methodology

Since this research work is done based on an existing building, the methodology of the research work developed accordingly. The methodology of this research will be composed of three steps;

- Identification of the building and interventions,
- Evaluation of the scenarios
- Analyzing the results of the scenarios for the best performance.

Identification of the Existing Building and Interventions

The case study building is oriented in the southern part of Istanbul as represented in Figure 2. The morphologic features of the selected area is mostly hilly and the average height above sea level is 190 meters. Istanbul has a mild weather, the winters are mostly rainy, with the temperatures in the range of 5-8 °C. Whereas, summers are warm and dry around averagely 25- 30 °C. The building was built as an elderly house in 2005 and the total conditioned floor area is 18.108 m2.

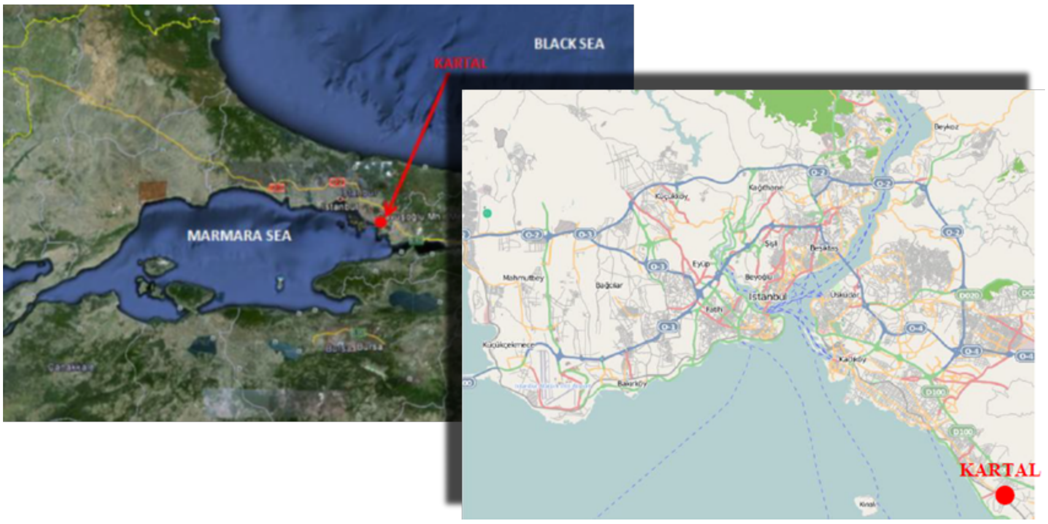

Figure 2. Demo building location in Istanbul

The existing building walls have two different characteristics:

- External walls of the residence rooms are insulated with 5 cm low density expanded polystyrene (EPS), yet, in most of the rooms material is either damaged or in a bad condition.
- External walls of the common spaces do not have any level of thermal insulation.

Building has a pitched roof with asphalt based water insulation and EPS thermal insulation. There are different types of windows in terms of glasses and window frames depending on the area of the building. Residential rooms are equipped with double glazed windows with aluminum frame and common areas have double glazed windows with vinyl frame. Residential rooms have also curtains to protect from extra solar radiation and heat gain as well as to respect residents' privacy.

Also as far as mechanical systems are addressed, two-pipe fan-coil units are used for heating and cooling purposes in the entire building. In addition to these systems, air handling units are used for heating, cooling & ventilation in the restaurant (located on fifth floor), in the swimming pool and the conference room (located on first basement floor). In the existing case, common spaces use fluorescence lamps while bedrooms use incandescent lamps. Fire protection sensors and electrical boards are located on each unit.

After identification of the existing building specifications, a set of interventions are proposed to enhance energy efficiency in the building. In the study, existing case conditions are improved by proposed interventions which are integration of insulation and replacement of lighting systems and windows. Also major renovation has done to improve the mechanical systems by integrating renewable systems such as solar thermal and heat pump systems as well as monitoring and controlling systems. All interventions are summarized in Table 1 in terms of Energy Conservation Measures (ECMs).

ECM1 and ECM6 thermal insulation application and windows replacement aim to improve thermal performance of the building envelope and accordingly reduce heat losses. Regarding insulation of envelope, four alternatives are investigated considering their specifications. Analysis results have shown that higher energy savings are provided by optimization of U-values. On the basis of the results, 0.327 W/m2K has been found out the optimum value for building's exterior wall. Whereas, considering replacement of glazing, ECM6 is accepted which includes all glazing; both resident windows and curtain walls. ECM2 includes application of radiant heating and cooling systems. The purpose of this intervention is reduce space heating loads with a modern and energy efficient system while providing comfortable indoor spaces which is called as radiant heating and cooling. Additionally, solar thermal system (ECM3) is accepted due to its high contribution potential. Simulations have suggested that installation of solar thermal system is beneficial for Istanbul climate in terms of producing DHW. Existing lighting system leads to inefficiency since existing building has incandescent lightings. Consequently, ECM4 which is LED lighting with sensor is determined due to its energy saving potential in terms of electricity. Energy automation and monitoring system application (ECM5) is another intervention that is applied to the demo building which offers an instant monitoring and controlling of the mechanical systems; consequently better automation.

Table 1. Interventions applied to the demo building

Interventions	**Code**
Thermal insulation application	ECM1
Radiant heating and cooling system application	ECM2
Solar thermal system application	ECM3
Efficient building appliances and lighting system (LED) application	ECM4
Energy automation and monitoring system application	ECM5
Windows replacement application	ECM6
Water saving systems application	ECM7
Geothermal heat pump application	ECM8

With respect to water saving system ECM7 is induced. The intervention includes grey water reuse, rain water reuse and installation of water efficient equipment. Lastly, heat pump application (ECM8) is considered to integrate renewable resources and accordingly enhance efficiency of the building by minimizing the thermal energy consumption.

Taking the all ECMs described and on the basis, six different scenarios combining different interventions are identified and given in Table 2.

Table 2. Identified energy scenarios based on the interventions

	ECM1	ECM2	ECM3	ECM4	ECM5	ECM6	ECM7	ECM8
Scenario 1	■							
Scenario 2	■		■			■		
Scenario 3	■		■	■		■		
Scenario 4	■			■		■		■
Scenario 5	■		■	■		■		■
Scenario 6	■	■	■	■	■	■	■	■

Evaluation Method of the Scenarios

After identification of the existing building and proposed scenarios, methodology is followed with evaluation of the scenarios. The detailed energy performance analysis of the building and systems are performed in dynamic simulation tools. Energy performance simulation programs are effective tools to examine energy performance and thermal comfort during the building's life-cycle (Maile, Fischer & Bazjanac 2007). Building geometry, weather condition and internal loads are the key parameters for accuracy of heating/cooling loads. Load calculation determines peak design loads for equipment and plant sizing. Accordingly, HVAC system is designed and energy consumption of the building is defined. It is very complicated to identify and integrate all the information regarding HVAC system, internal loads, operating strategies and schedules for this kind of big scale and multi-zone building. To combine all the multidisciplinary systems and related information together in one programme requires expertise not only about systems but also about applied software. EQuest, which is widely used building energy simulation software based on DOE-2 engine, is selected as base analysis software for this study because it is user friendly and allows to configure different building systems and combine them. Energy simulation tools predict the energy consumption of a given building and thermal comfort of its occupants. Based on the parameters given in Figure 3, EQuest performs a dynamic hourly simulation for a one year period, 8760 hours.

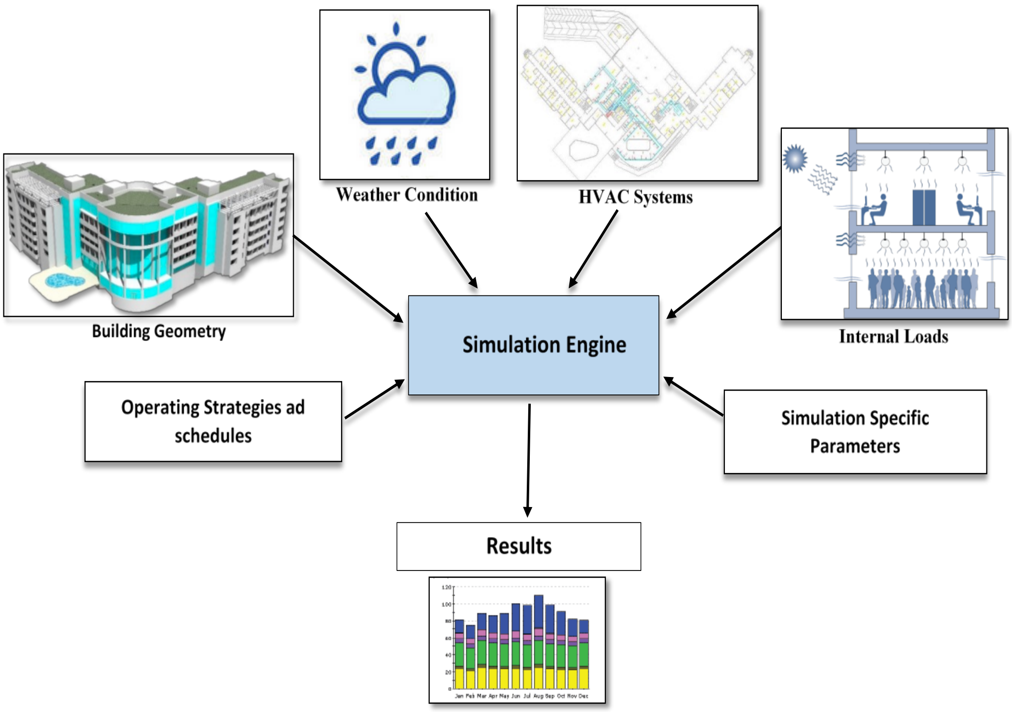

Figure 3. EQuest simulation engine

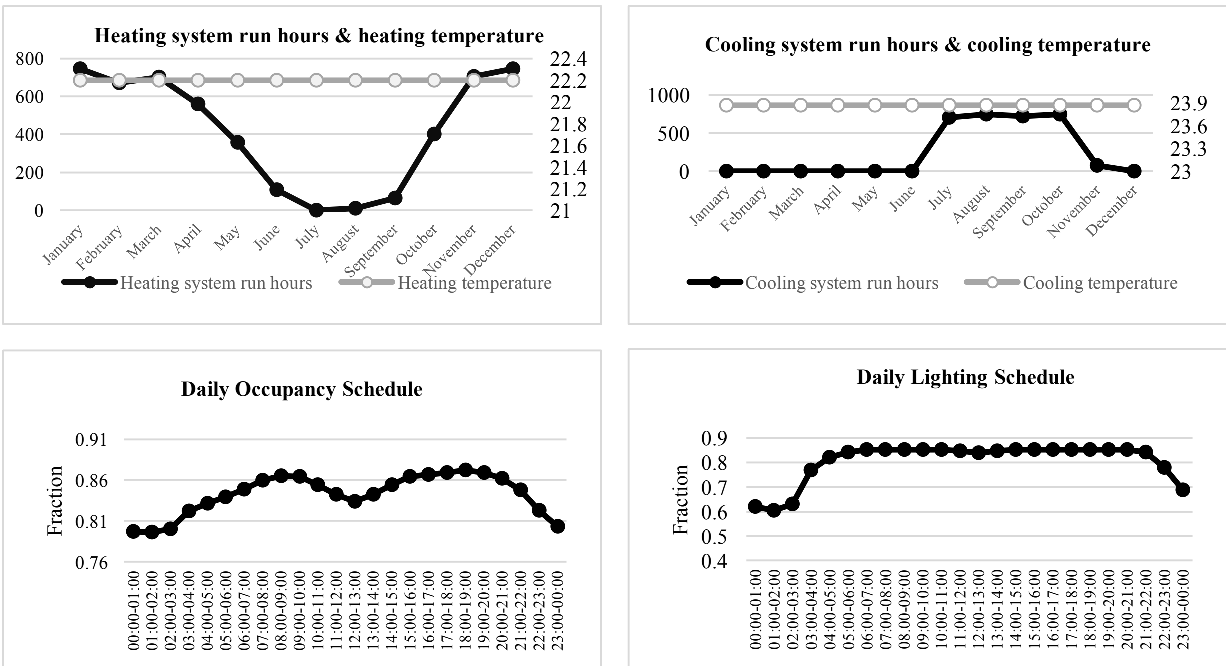

Figure 4. Schedules for occupancy, HVAC and lighting systems

As it is indicated in the Figure 4, building geometry, weather condition and internal loads are the key parameters for accuracy of heating/cooling loads. Load calculation determines peak design loads for equipment and plant sizing. Accordingly, HVAC system is designed and energy consumption of the building is defined. Considering schedules and thermal properties of building envelope according to actual state, which are illustrated in the Figure 4 and Table 3, building simulation model has been created.

Table 3. Thermal properties of the building envelope

	Exterior walls	Underground walls	Roof	Floor	Windows
U-value (W/m^{2}K)	0,327	0,482	0,4	2,4	1,6

Analyzing results of the scenarios for the best performance

In the evaluation phase, generation of the simulation model is explained. All factors that affect heating and cooling loads are modelled in detail to get precise results for the energy consumption. After building's simulation model generation, the model is performed to get both existing condition's and energy scenarios' results. Simulation model of the building is represented in Figure 5.

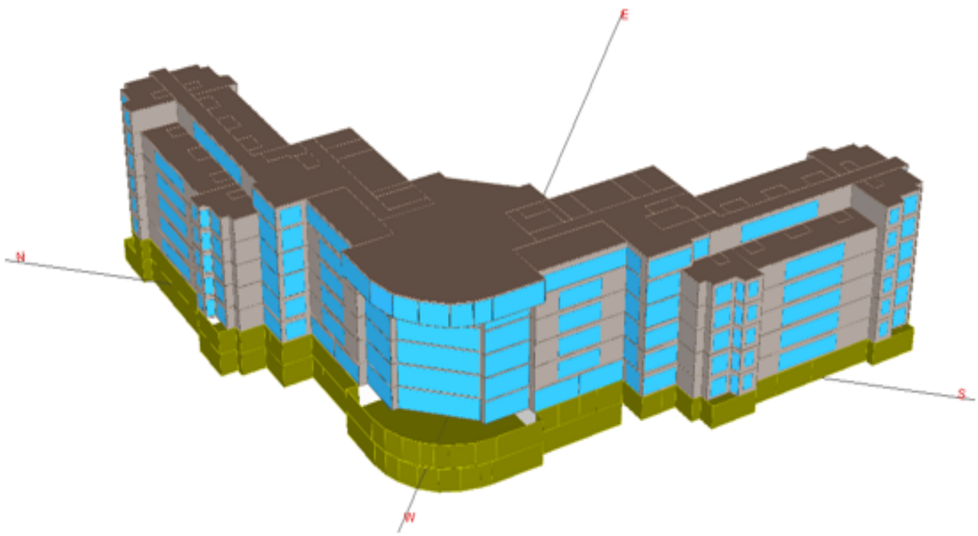

Figure 5. Simulation model of the building

Results are collected under varied titles such as lighting, misc. equipment, space heating, space cooling, pumps, ventilation fans domestic hot water (DHW).

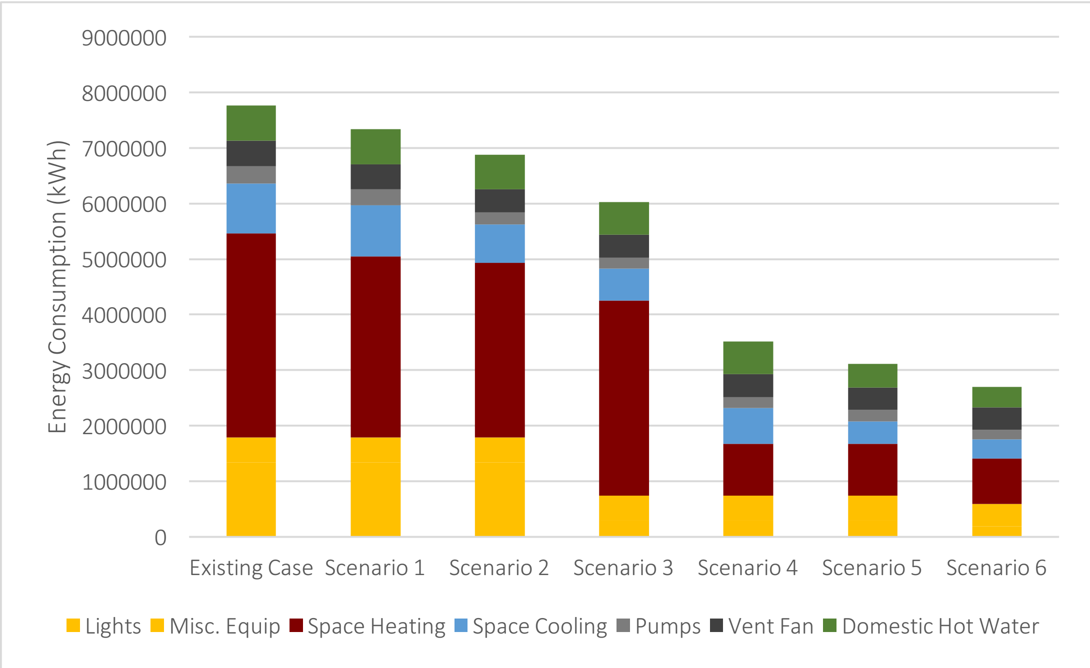

Figure 6. Total annual energy consumption of the existing case and scenarios

As a result of proposed interventions in this research, more than 60% energy performance improvement and correspondingly a 70 kg/m^{2}year approximate greenhouse gas emission reduction are estimated throughout whole year period. Energy consumption breakdown on the basis of scenarios is represented in Figure 5 as it follows.

In addition to lighting systems, building thermal energy systems are renovated. As other researches have revealed, geothermal heat pumps offer up to 30-55% efficient systems based on climatic conditions and application (Morrone, Coppola & Raucci, 2014; Self, Reddy & Rosen 2013). Similarly, in this study, scale of the thermal consumption is reduced dramatically due to the integration of the heat pump system to the building in Scenario 4. In the baseline case all the heating was being covered with the conventional boilers that works with natural gas. As a consequence of geothermal and air source heat pump installation, thermal peak load of the building is reduced substantially. Renewable heat pump systems that use site ground water have led approximately 50% efficiency in thermal consumption in comparison with the existing conditions. In addition to new HVAC system, solar thermal applications are applied for domestic hot water preparation. According to researches, climatic conditions are highly favourable for solar thermal applications especially for hot water heating in the region. (Benli, 2016) Consequently, in Scenario 5, solar thermal collectors are placed to the building. Integration of solar thermal technologies has increased the efficiency by lowering DHW consumption by 33%, as results have proved. Finally, Scenario 6 which is the combination of all proposed interventions has been found out to be the best scenario for the building with approximately 60% less energy consumption compare to the existing case of the building.

Conclusion

The research emphasizes the significance of sustainable development in the city environment which is very complex and requires advanced integration of building systems and interventions in different categories. The findings of this investigation have a number of important implications for future practice. Both existing condition of the case building and defined interventions are identified based on its critical parameters and explained in detail. The result of each scenario showed that there is dramatic reduction on total energy consumption of the building. As illustrated in the results, improvement on energy was basically coming from the integration of major energy sources (such as heat pump systems, solar collectors or LED) which was the result of major building renovation. With the careful design strategies of all the mentioned building systems final energy consumption reduction is up to 60%. In comparison to other studies referred in this study, the saving percentage is convenient since it is an outcome of major renovation works; both in the field of building envelope and integration of an advanced building system. This value can be taken into account as a representative percentage of how energy consumption can be diminished in such big scale buildings that have different types of systems. Another critical issue to get this dramatic improvement is that the applied interventions are mainly depend on renewable sources. This also has major effect on the environmental index by reducing the CO2 emissions. 70 kg/m^{2}year approximate greenhouse gas emission reduction is expected within the renovation activities.

Acknowledgements

This paper is produced based on a FP7 project called "R2CITIES: Renovation of Residential urban spaces: Towards nearly zero energy CITIES, Grant Agreement No: 314473".

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5

Life Cycle Impact Assessment Analysis on a Cooling System

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Yavuz Özçelik
Nazlı Yaşar Tunca

Abstract

The system that was investigated within this chapter consists of two subsystems one of which are the absorption cycle where cooling is produced and the heat production subsystem where the required heat is supplied to the first system as hot water. The function of a solar assisted absorption system is to produce ***100 kW*** *cooling. Solar radiation is the main heat source of solar cooling systems. The goal of using these systems in real life is to produce cooling and to determine the environmental and economic performance of the solar cooling system following the Life Cycle Assessment (LCA) methodology. The Eco-indicator 99 accounts for 10 different categories such as carcinogenic effects, climate change, ionizing radiation, ozone layer depletion, respiratory effects, acidification and eutrophication, toxic emissions, land occupation, extraction of minerals, extraction of fossil fuels that are combined under three types of damages which are human health damages, ecosystem quality damages, damages to resources. Minimum and maximum total costs are calculated as 2034346.08€ and 3366998.48€, when total environmental impacts are at its maximum and minimum which are 280633.14 and 70652.09.*

Keywords: Life Cycle Assessment; Absorption Cooling System; Solar Assisted cooling system; environmental impacts

Introduction

Cooling demand is rapidly increasing in many parts of the world, especially in moderate climates. The temperature can reach up to 40-45 °C in various regions of Turkey. The scientists announced that due to the global warming, the average global temperature has increased 0.6 °C during the 20th century. Also, the average global temperature rise is predicted to be between 1.4 and 5.8 °C until the year 2100, unless the emission of greenhouse gases is avoided. This results in a dramatic increase in electricity demand in hot summer days, which threatens the stability of electricity grids and causes an unwanted increase in the use of fossil fuels and nuclear energy. Current fossil-fuel based energy supply systems are not sustainable as they contribute substantially to the climate change and mainly depend on the resources of only a few countries. Hence, energy research can play an essential role in finding solutions to current environmental problems and fulfilling the need for more sustainable cooling systems (Tunca, 2014).

Solar radiation is the main heat source of solar cooling systems. However, as solar radiation is variable due to the seasonal changes, additional back-up heat sources may be integrated to the system such as fossil fuel or waste heat recovered from other thermal systems. Although, absorption technologies have many environmental advantages, they have the drawback a higher capital cost compared to conventional compression systems since they include higher number of units for the required heat production subsystem, which includes the solar collectors as well as the auxiliary heating system along with the absorption cycle itself (Gebreslassie, et.al,2009b). Because solar cooling is not yet widely used and available, the awareness of solar cooling will become a key to the growth in the near future. It is important to understand its barriers to growth and develop solutions to optimize the performance of these systems taking into account also their environmental impact in order to become a real alternative.

Literature Review

Many studies were performed on modeling and simulation of solar assisted absorption coolers and also there are many studies are present in the literature on the improvement of performance of these systems.

The energy and environmental performance of solar thermal collectors for sanitary warm water demand following Life Cycle Assessment methodology considering production process of the collectors, installation, maintenance, transports and disposal has been studied by Ardente et al. (2005).

Solar assisted absorption cooling systems can be improved by integrated heating system. Mateus et al. (2009) evaluated the potential of integrated solar absorption cooling and heating systems for applications in different building types and in three different locations; Berlin, Lisbon and Rome. According to Mateus, minimum costs depend on the building type and location. Additionally, the single-family house and the hotel are the building types that the system has higher economic feasibility. They also pointed out that, although the operation cost of integrated solar assisted cooling and heating systems are lower compared to conventional systems, the total cost including the investment, operation and maintenance costs is much higher.

Gebreslassie et al. (2009b) performed an economic analysis for the design of an absorption cooling system under uncertainty in the energy cost the solution to which is given by a set of pareto optimal solutions via the epsilon constraint method.

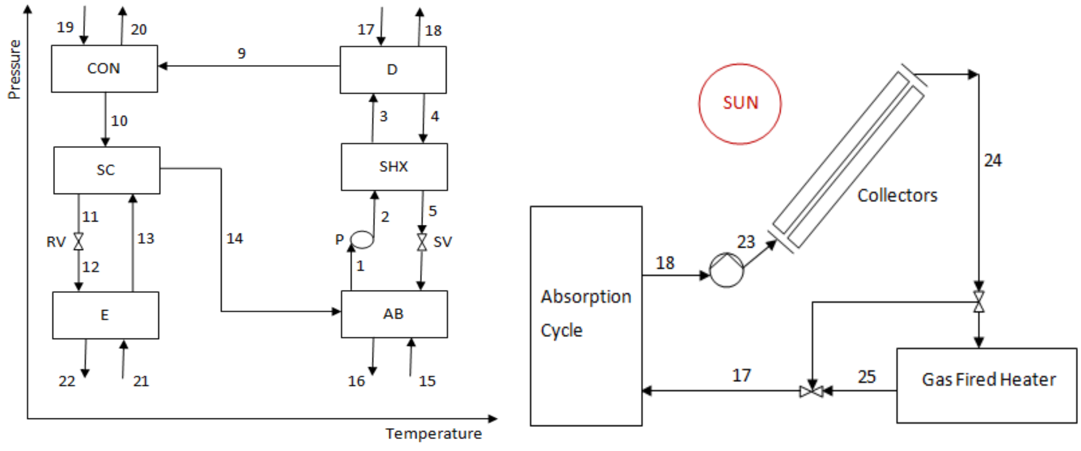
Hong et al. (2010) indicates that the coefficient of performance of a single effect absorption refrigeration cycle system can be improved by introducing an expander-compressor.

The global warming potential of solar assisted absorption cooling systems are studied by Gebreslassie et al. (2012). They concluded that without considering governmental subsides, the use of solar energy for cooling applications is not profitable. In another study, Gebreslassie et al. (2010b) addressed the minimization of the total cost of a solar assisted absorption cooling system and its associated total life cycle impact accounting for the damage caused in all the stages over its entire life span. They showed that significant reductions in the environmental impact can be achieved when solar collectors are used.

Operation Principle of Solar Assisted Cooling System

In this study, the equipment of absorption cycle (Figure 1-a) are the absorber (AB), condenser (CON), desorber (D), evaporator (E), refrigerant sub cooler (SC), refrigerant expansion valve (RV), solution heat exchanger (SHX), solution pump (P) and solution expansion valve (SV). The vapour refrigerant (Stream 9) is separated from water by heating the concentrated water-refrigerant solution in desorber under high pressure and then condensed completely in condenser. The liquid refrigerant (Stream 10) is sub cooled (Stream 11) in the sub cooler by the superheating stream (Stream 13) coming from evaporator. The liquid refrigerant flows through refrigerant expansion valve so the pressure is decreased and then evaporated under low pressure by the heat taken from the environment. The vapour refrigerant (Stream 13) is heated by stream 10 and enters to the absorption column. The refrigerant is absorbed in the weak water-refrigerant solution and leaves the column as a rich solution (Stream 1). The absorption process is exothermic therefore, the absorber requires constant cooling to maintain in its temperature. Stream 1 passes through pump and enters to the solution heat exchanger to be heated by weak solution (Stream 4) before entering desorber. Stream 3 enters to the absorber, heated by the hot water coming from solar collector part in order to separate the refrigerant from water. Since the boiling point of the ammonia is lower than water (-33 ^{0}C) almost all of the ammonia is evaporated with a trace amount of water. The fraction of ammonia is estimated to be constant at 0.99. Streams 15-22 are external heat transfer fluids. Stream 17 carries the required hot water from the heat production system and stream 18 brings back the cooled water in order to be heated.

The solar system where solar collectors and auxiliary heating system which is a gas fired heater operating with natural gas, is demonstrated in Figure 1-b.



a) *b)*

Figure 1 Absorption cycle (a) and solar system (b)

Life Cycle Assessment

Life cycle assessment (LCA) is one of several environmental management techniques. Risk assessment, environmental performance evaluation, environmental impact assessment analyses are other examples of environmental management techniques. According to ISO Standard (Iram-Iso 14040, 2006), LCA is a technique for assessing the environmental aspects and potential impacts associated with a product. LCA studies the environmental aspects through a product's entire life span. The life begins with the gathering of raw materials from the earth and ends at the point when all the materials return to earth.

LCA Phases

LCA has four main phases and these phases are required to be defined clearly. The phases may have feed backs and feed forwards between each other.

In **Goal and scope definition** phase the reason of LCA analysis should be clearly defined. To whom the results of the study may affect shall be established. The following descriptions should be defined well to understand the goal and scope of the study.

The **Function of a system** is the main purpose of its usage. According to ISO 14040 the functional unit is defined as measure of the performance of the functional outputs of the product system. The primary purpose of a functional unit is to provide a reference to which the inputs and outputs are related. In this study the function of a solar assisted absorption system is to produce **100 kW** cooling.

The **System boundaries** determine which unit processes shall be included within the LCA. The selection of the inputs and outputs are shall be consisted with the goal of the study. An input and output is described as the material or energy that enters and leaves a system, respectively.

Data quality requirements specify in general terms the characteristics of the data needed for the study. Since the selected data affects directly the results of the study, the selection of the data is important. The data quality should address;

- The time coverage that the data is valid,
- The geographical area that the data covers,
- The technology that the data represents,
- The production group that the data covers etc.

Performing an LCA can be resource and time intensive. Depending upon how thorough an LCA the user wishes to conduct, gathering the data can be problematic, and the availability of data can greatly impact the accuracy of the final results. Therefore, it is important to weigh the availability of data, the time necessary to conduct the study, and the financial resources required against the projected benefits of the LCA.

Life Cycle Inventory Analysis (LCI)

Inventory analysis involves data collection and calculation procedures to quantify relevant inputs and outputs of a product system. These inputs and outputs may include the use of resources and releases to air, water and land associated with the system (e.g., air emissions, solid waste disposal, and waste water discharge). The data collection shall be performed for each unit process included in the system boundaries (Tunca, 2014).

Life Cycle Impact Assessment (LCIA)

In this phase the potential environmental impacts are evaluated using the results of inventory analysis. The impact categories point out the areas that the product or system affects (e.g., climate change, ozone layer depletion, carcinogenic effects etc.). The impact assessment phase may include the following elements (Iram-Iso 14040, 2006);

- Assigning of inventory data to impact categories (classification)
- Modeling of the inventory data within impact categories (characterization)
- Possibly aggregating the results in very specific cases and only when meaningful (weighting).

The environmental performance is measured by the Eco-indicator 99 metric taken from Ecoinvent Database. Ecoinvent supplies Life cycle inventory (LCI) data and offers science based, industrial, international life cycle assessment (LCA) and life cycle management (LCM) data and services (Ardente, 2005, The Ecoinvent Center, 2011, Tunca, 2014).

Results and Discussion

Construction and operation stages of evacuated tube collector (ETC) are considered for the evaluation of environmental impacts. For the construction stage, 1m^2 ETC production is selected and for operation stage, this selected ETC is used for the production of 1 MJ heat.

As can be seen from the Figures 2 and 3, the impact points of construction of ETC are higher than impact points of operation for a delivery of 1 MJ of useful heat at collector. Nevertheless, manufacturing is accounted only once while operation impact will depend on the total heat generated.

In manufacturing part, the impact that threats resources have the highest point. This is mainly due to large amounts of extraction of ferrous minerals used in manufacturing. The damage category of resources is followed by the human health category. The reason for this is the significant amount of emissions to the air.

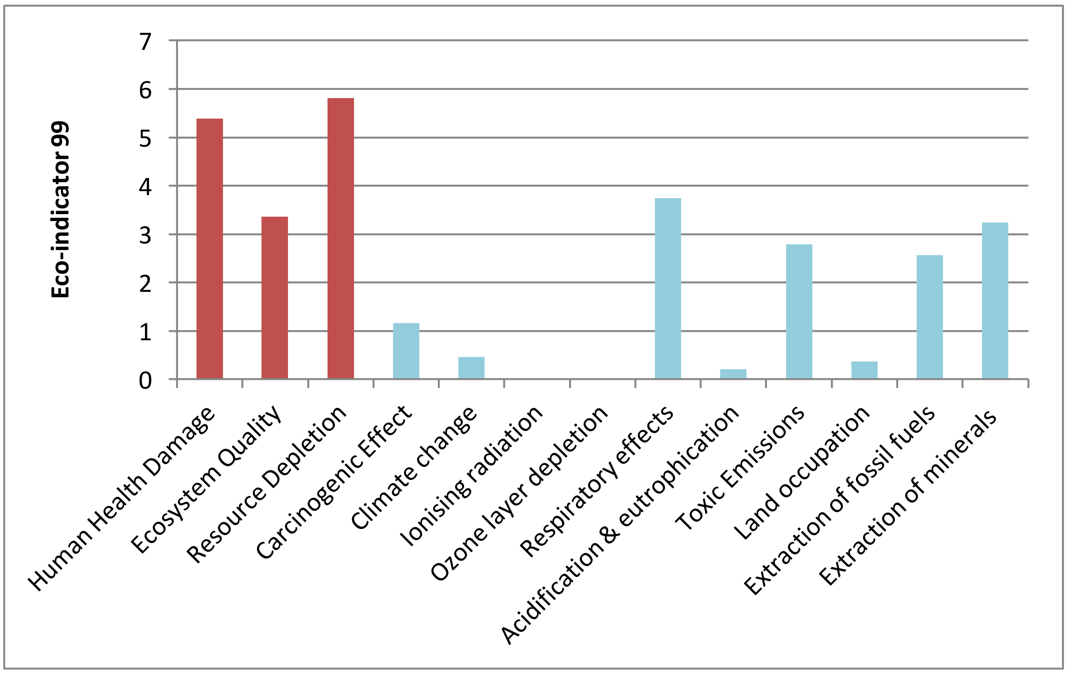


Figure 2 Impact points for the construction of 1m^2 evacuated tube collectors

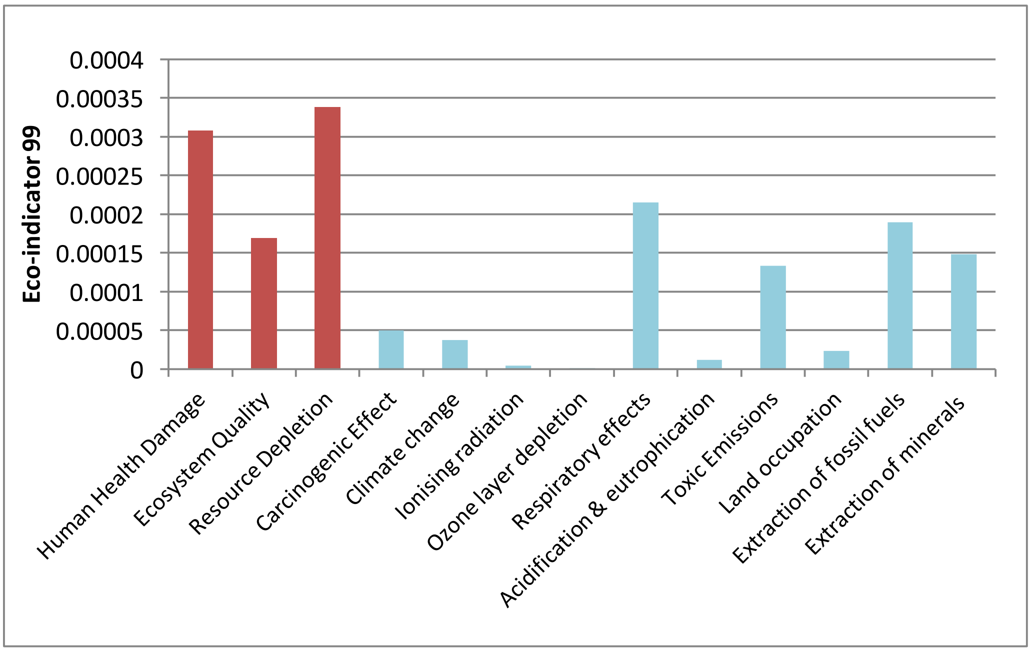


Figure 3 Impact points of operation of ETC per 1MJ of heat produced

Air emissions during the production of collectors include mostly CO_2 emission, indirect emissions related to the raw material production and direct emissions of some metal pollutants consisting of iron, manganese, chromium and molybdenum etc. related to the dominant production processes which are plasma cutting, coating and welding.

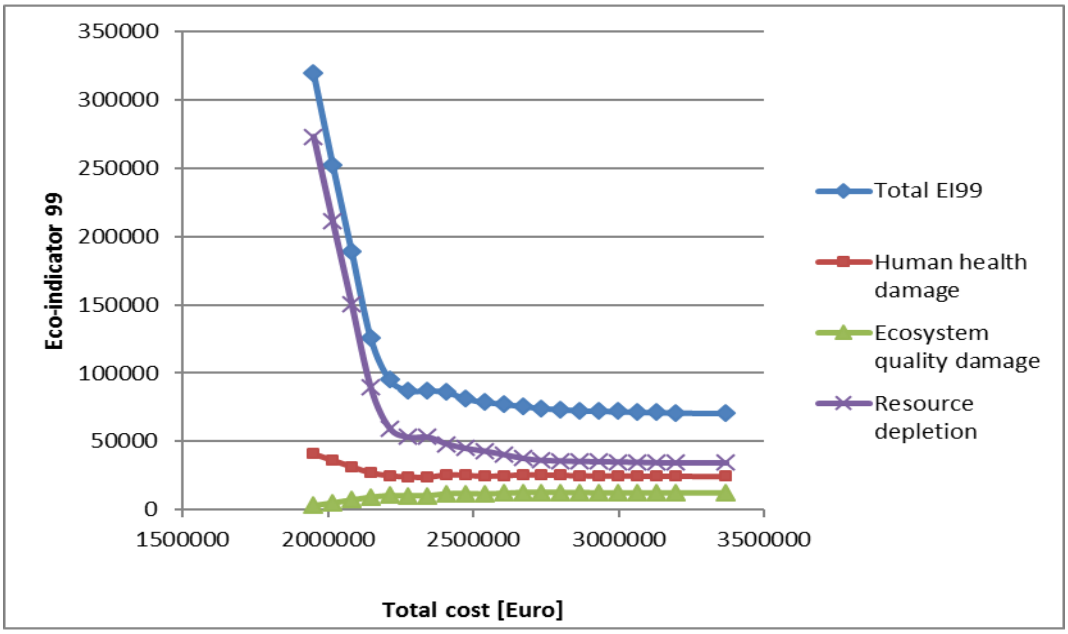


Figure 4 Pareto set of optimal solutions for total environmental impact (Total EI99) and corresponding damage categories.

The same order of impact points is observed in the operation part. The Eco-indicator 99 of the operation part is considered for the delivery of 1 MJ of heat at collector including the necessary auxiliary heating, maintenance and electricity use for operation. In order to produce high amount of heat at collectors, more electricity is consumed to operate the pump in the collector part.

The total environmental impact and total cost are minimized simultaneously and the set of Pareto solutions that satisfy both objective functions are shown in Figure 4. Three damage categories that correspond to each Pareto solution are presented in the same figure as well. It is obvious that there is a trade-off between total cost and environmental impact. Concerning the damage categories, damage to natural resources follows the same tendency of total environmental impact. This is quite easy to understand because the minimum point of total impact corresponds to a design with many collectors that supply heat to the cycle and they contribute to less fossil fuels utilization. Also, it should be noticed that resource depletion and human health damage has similar tendency as the total Eco-indicator, whereas ecosystem quality damage has an opposite direction that increases as total impact decreases. The reason for this is the emissions of heavy metals associated with the manufacture of solar collectors as mentioned before. The emissions of these metals have ecotoxic effects and thus lead to an increase in ecosystem quality.

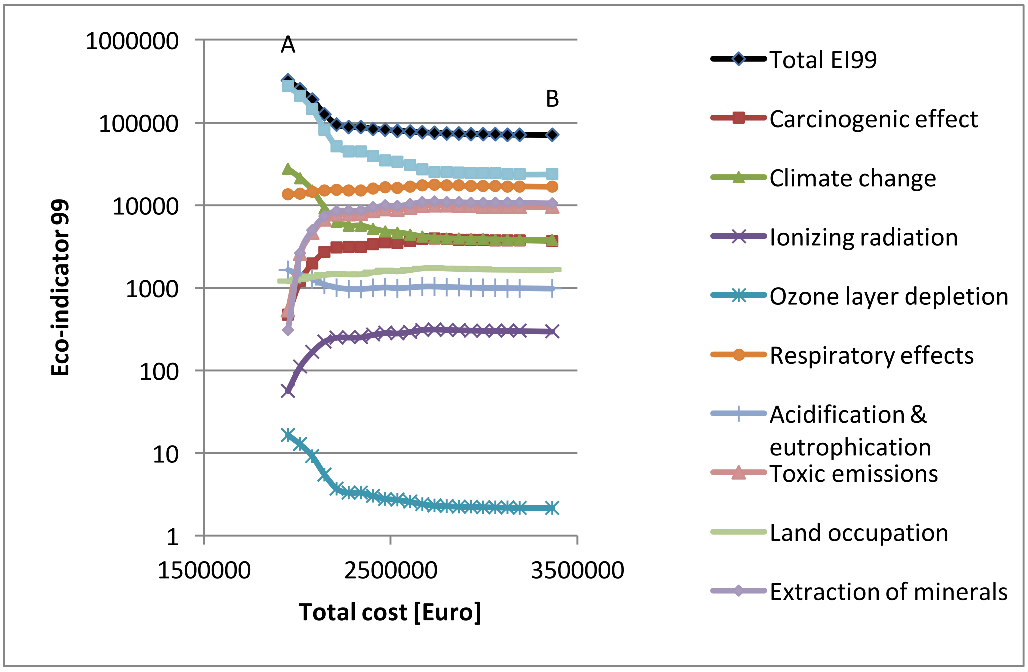


Figure 5 Set of solutions for minimum total Eco-indicator 99 and corresponding environmental impacts

Figure 5 presents the details on the impact categories for the Pareto curve corresponding to the total environmental impact – total cost objective function. Logarithmic scale is used in the following figures to show tendencies of all impacts, as their order of magnitude can be very different. It can be observed from the Figure 5 that, some of the impact categories have lower values in the minimum cost solution; however, the opposite happens for other impact categories. Points A and B represent the minimum cost and minimum environmental impact designs, respectively. In both designs ozone layer depletion makes the lowest contribution to the total impact. This is due to the fact that instead of CFC's and HCFC's, water and ammonia are used as working fluids in the system. In any case, it can be seen that the main contributors to the total environmental impact are extraction of fossil fuels and climate change in the minimum cost design and respiratory effects in the minimum environmental impact design.

In Table 1, the number of collectors, total area of collectors and total area of the cycle at each minimum point of impact category, total cost and total Eco-indicator 99 can be seen. It is observed that, 630 solar collectors exist in the design of minimum total environmental impact, climate change, ozone layer depletion, acidification and eutrophication and extraction of fossil fuels. However, no collector is chosen in minimum solutions of the rest functions.

Figure 6 depicts the contribution of several parameters and units (shown in the right hand side of the figure) for each minimum impact category designs. The impact for the pump, which is the solution pump in the absorption cycle, includes the sum of construction and electricity consumption for its operation. In the minimum carcinogen, ionizing radiation, respiratory effects, toxic effects, land occupation, mineral extraction and minimum cost solutions the main contributor to those impact categories is natural gas. In these solutions where there are no solar collectors, natural gas is burned to supply the required heat for the cycle. Since the pump consumes more electricity to circulate the solution in absorption cycle, it also contributes to total of each impact category.

Table 1 Associated number of solar collectors, total area of collectors and the total area of equipments in the absorption cycle with minimum solution of total environmental impact, total cost and each impact category

Minimization of each category	Number of Collectors	Total Area of Collectors (m^2)	Total area of the Cycle (m^2)
Total EI99	630	619.9	799.1
Total Cost	0	0	97.4
Carcinogenic effect	0	0	97.3
Climate Change	630	619.9	801.4
Ionization Radiation	0	0	97.4
Ozone Layer Depletion	630	619.9	802.7
Respiratory Effects	0	0	97.4
Acidification and Eutrophication	630	619.9	854.3
Toxic Emissions	0	0	97.4
Land Occupation	0	0	97.4
Extraction of Fossil Fuels	630	619.9	802.8
Extraction of Minerals	0	0	97.4

In Figure 7, normalized values of each impact are plotted in ordinate and the set of objective functions are shown in x axis. Normalization is performed by dividing each solution of objective function by its maximum. Each line corresponds to a different design and associated normalized impact values of each of the 10 category, total Eco-indicator and total cost. As an example; the brown line with square markers corresponds to the design with minimum total cost, minimum carcinogenic effect, minimum ionizing radiation, minimum respiratory effects, minimum toxic emissions, minimum extraction of minerals, while at the same time maximum climate change, maximum ozone layer depletion, maximum acidification and eutrophication, maximum extraction of fossil fuels and maximum total environmental impact. Also, the line with circular markers corresponds to the design with maximum cost where there is minimum environmental impact. The other curves correspond to intermediate solutions of all functions. It is interesting to notice that, one can reduce total environmental impact 75%, extraction of fossil fuels 77%, climate change and ozone layer depletion 76% by increasing total cost approximately 20% as can be seen from the line with triangular markers.

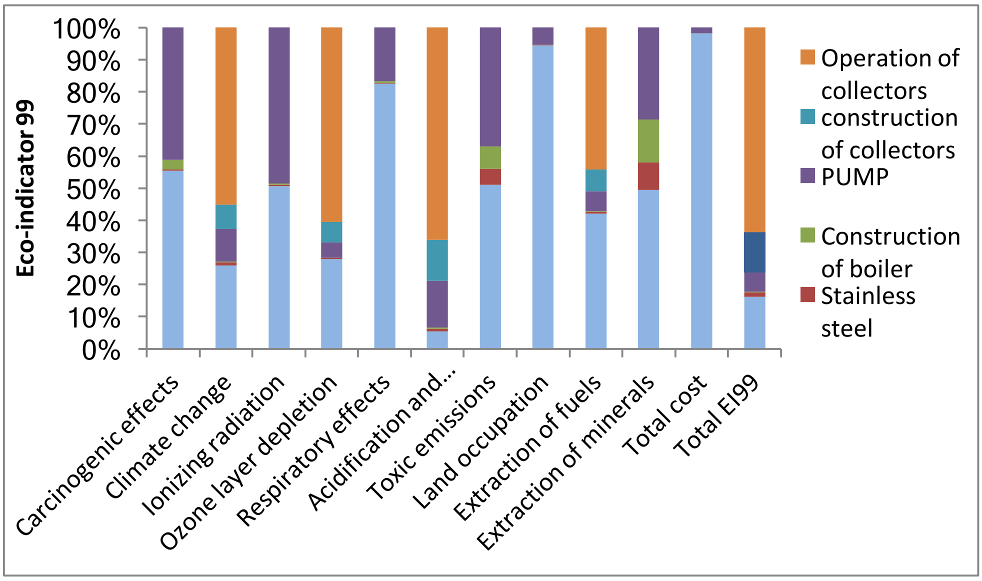
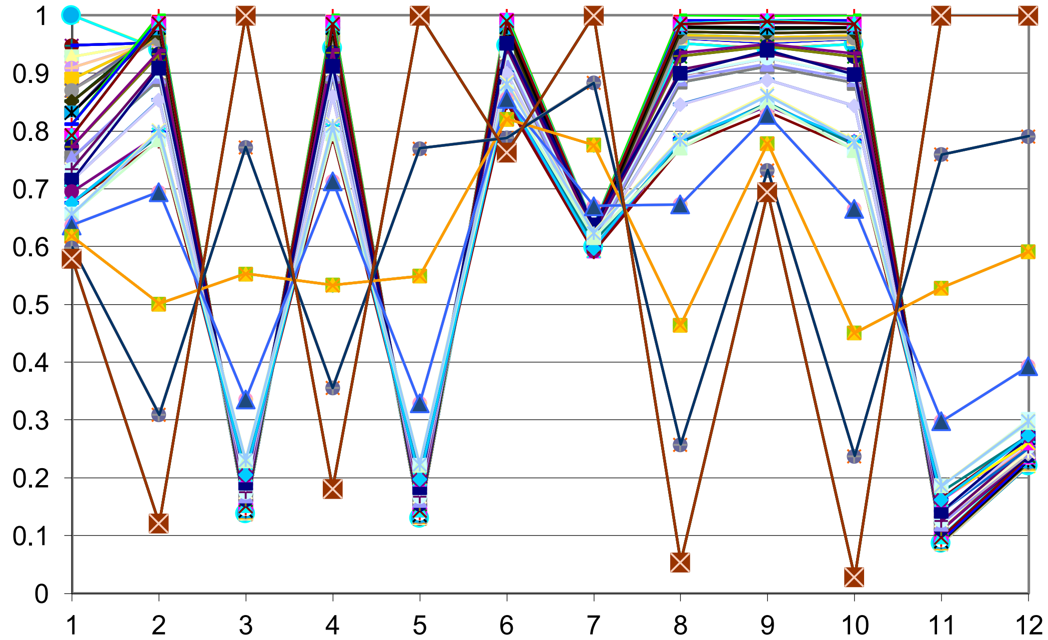


Figure 6 Contribution of several parameters to the total impacts at minimum points of each single impact.



** 1: total cost, 2: carcinogenic effects, 3:climate change, 4: ionizing radiation, 5: ozone layer depletion, 6: respiratory effects, 7: acidification and eutrophication, 8: toxic emissions, 9: land occupation, 10: extraction of minerals, 11: extraction of fossil fuels, 12: total environmental impact.*

Figure 7 Two-dimensional Pareto sets in parallel coordinates

Conclusion

In this study, the environmental performance analysis of a solar assisted absorption cooling system is presented based on formulating a nonlinear programming (NLP) problem. It is aimed to minimize total environmental impact and 10 single impact categories simultaneously with total cost using the Eco-indicator 99 metric. LCA principles have been used while performing environmental analysis.

It has been shown that there is an obvious trade-off between total cost and total environmental impact, damage to climate change, ozone layer depletion, acidification and eutrophication and damage to fossil fuels. This is accomplished by introducing more collectors to the system. On the other hand, after optimizing the rest of the impact categories simultaneously with the total cost, the solutions are not presented by a Pareto curve but by one minimum point since those functions have a similar trend as the total cost.

Minimum total cost is calculated as 2034346.08 € when total environmental impact is at its maximum which is 280633.14. The minimum total environmental impact is calculated as 70652.09 when the total cost is at its maximum value which is 3366998.48 €. It is clear that there is a conflict between total cost and environmental impact. As the environmental impact decreases, the total cost of the system increases. Decision makers can choose the best design according to their requirements and environmental constraints.

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6

Performance Analysis of a Cascade Refrigeration System with the Replacement of HFC Refrigerants with Natural Ones

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Abstract

The replacement of synthetic refrigerants such as R132a or R404A in refrigeration applications with natural ones gains recently more attention due to their harmful effects on environment. Conversely, these refrigerants have better thermo-physical properties than the natural ones. Therefore it is important to compare performance of the systems operating partially or fully with the natural refrigerants with that of synthetic refrigerants. Moreover, an appropriate selection of refrigerants to operate the low and high temperature cycles should be made in order to obtain high coefficient of performance (COP) besides lowering the trace of the refrigerants on the environment during operation, leakage and recharge. For this purpose, one solution may be using CO_2 in the low temperature cycle (LTC) of the refrigeration system whereas the high temperature cycle(HTC) of a cascade refrigeration system may use ammonia, propane or R404A. First two proposals represent fully natural refrigerant solution however the last option corresponds to partial use of natural refrigerants. In this study, the performance and the environmental considerations of three different refrigerant pairs in a cascade refrigeration have been investigated. CO_2 is assumed to be the refrigerant of LTC while HTC refrigerant is varied from partially to fully natural refrigerant options. In order to realize an energy efficient and environmentally friendly refrigeration system, CO_2/R404A, CO_2/NH_3 and

CO_2/R290 pairs of refrigerants are examined. Their performances and mass flow requirements are analyzed and compared for different operating conditions.

Keywords: Cascade system, Natural refrigerants, Performance coefficient

Introduction

Conventional refrigerants are being phased out worldwide because of the risk of ozone layer depletion (ODP) and global warming potential (GWP) considerations. Natural refrigerants are increasingly used in low temperature refrigeration applications. Mainly, carbon dioxide, ammonia, propane and other natural refrigerants have drawn increased attention as refrigerants to protect the environment. The cascade refrigeration systems including low and high temperature cycles are commonly applied to reach low and very–low temperature levels. In design of such systems, the temperature levels in low and high temperature cycles are important parameters determined from the ambient conditions and desired cooling space temperatures. In order to decide the best refrigerant in the application, along with the design conditions other important characteristics such as toxicity, flammability, ODP, GWP etc. should be also taken into account.

There has been a significant interest in two-cycle cascade systems during the past decade, particularly with the increasing the popularity of CO_2 as a low temperature refrigerant. CO_2 has several advantages compared to other refrigerants because it is a non-toxic, non-explosive and environmental friendly. In addition, the size of the units in the refrigeration system with CO_2 is more compact due to its lower specific volume accompanied with higher operating pressure values.

There are several studies in literature using CO_2 and different synthetic refrigerants such as R22, R290, R1270 and R404A in cascade refrigeration applications (Bansal and Jain 2007; Bansal 2012; Bhattacharyya et al. 2005; Messineo 2012; Da Silva et al. 2012; Yilmaz et al. 2014).

Bansal and Jain (2007) evaluated the optimum cascade condensing temperatures of R744 of the low temperature refrigerant for different refrigerants such as R717, R290, R1270 and, R404A, which are in the high temperature cycles of a cascade system. They concluded that CO_2 is a potential low temperature refrigerant for temperatures less than -50°C due to its low cost and promising properties. Also, ammonia is the best high temperature cycle refrigerant if it is located outside of the building. Bansal (2012) presented that a comprehensive summary on the outgrowth of CO_2 as the most promising refrigerant for low temperature applications. Particularly, CO_2 perform up to 60% better than the conventional single stage supermarket refrigeration systems operating with R404A. Bhattacharyya et al. (2005) studied a carbon dioxide-propane (R744–R290) cascade system in order to determine the optimum cascade evaporating temperature of R744 in the high temperature cycle. Messineo (2012) has carried out the thermodynamic analysis of a R744/R717 cascade refrigeration system and of a R404A two-stage system at the same working conditions. He reported that a R744/R717 cascade refrigeration system is a remarkable alternative to R404A two-stage refrigeration system for low evaporating temperatures such as -30ºC and -50ºC. Da Silva et al. (2012) presented a comparison of R404A/CO_2 cascade system with single-stage systems of R404A and R22 in a supermarket application operated at the evaporation temperature of -30ºC. They concluded that the cascade system can reduce energy consumption and refrigerant charge compared to the single stage systems. Yilmaz et al. (2014) examined influence of different operating conditions on a R404A/CO_2 cascade system performance and determined the optimum operating conditions to maximize the COP and thereby minimize the exergy destruction of the system.

In the present study, the best refrigerant pair for a cascade refrigeration cycle has been investigated for three different cases. CO_2 is assumed to be the refrigerant of LTC while HTC refrigerant is varied from partially to fully natural refrigerant options. In order to realize an energy efficient and environmentally friendly refrigeration system, CO_2/R404A, CO_2/NH_3 and CO_2/R290 pairs of refrigerants are examined. Their performances and mass flow requirements are analyzed and compared for different operating conditions.

Thermodynamic analysis of a cascade system

In a two-stage cascade system, two independent refrigeration cycles are paired through a heat exchanger named a cascade condenser, where the heat transfer between two cycles occurs. Figure 1 shows schematic diagram of the two-stage cascade refrigeration system. In a cascade condenser, the refrigerant vapors of the low temperature cycle are condensed whereas the liquid phase refrigerant of the high temperature cycle are evaporates. Therefore, it operates at intermediate pressure and temperature as evaporator for the high temperature cycle and condenser for the low temperature cycle. In a single cycle refrigeration system there are two temperature levels, the evaporating temperature and the condensing temperature which are represented by T_E and T_C, respectively. As expected, these temperature levels depend on the temperatures of both the conditioned space and the ambient conditions. On the other hand, in a cascade system there are four temperature levels; the two additional temperatures being the condensing temperature of the low temperature system, $T_{CAS,C}$, and the evaporating temperature of the high temperature system, $T_{CAS,E}$. These temperatures between the high and low temperature cycles are a design parameter which plays an important role in determining the coefficient of performance (COP) of the overall system.

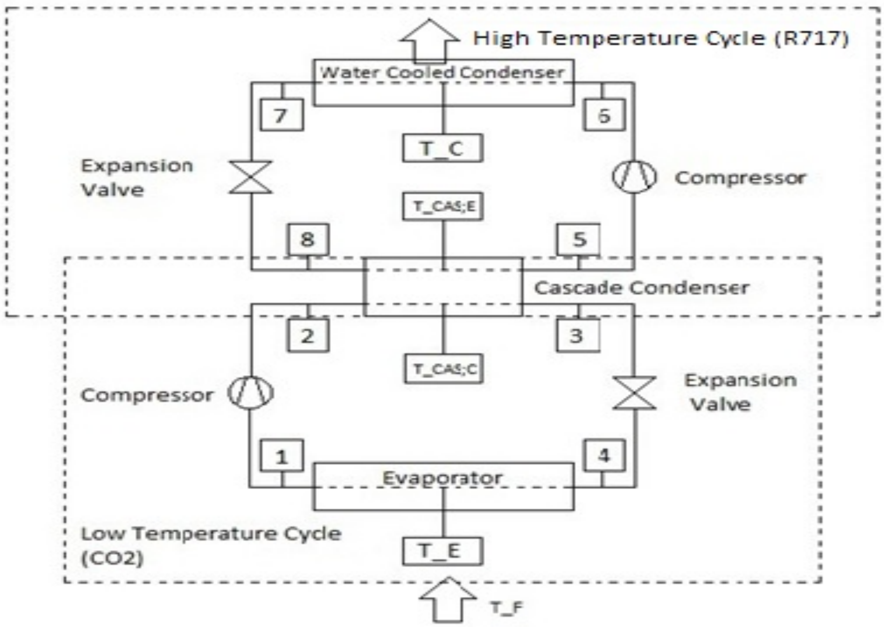

Figure 1. Schematic of a two-stage cascade refrigeration system

The thermodynamic model of the cascade system is developed using first law of thermodynamics. Mass, energy equations are derived for both low and high temperature cycles. In this study, considering the schematic and state points of Figure 1, the following equations are used for the analysis. The coefficient of performance (COP) and the mass flow ratio of two cycles are computed for various operating conditions.

Following assumptions are taken into consideration in the analysis.

- isenthalpic expansion of refrigerants in expansion valves,
- isentropic compressor efficiencies of 0.80 both low and high temperatures cycles,
- potential and kinetic energy changes are neglected,
- heat and pressure losses in all components are neglected.

Numerical calculations are performed using well-known Engineering Equation Solver (EES) software. EES is a general equation-solving program that can numerically solve coupled non-linear algebraic and differential equations. The thermo-physical properties of the refrigerants (CO_2, NH_3, R290 and R404A) specified in this study is obtained using EES which has property database of numerous refrigerants.

The mathematical model of the cascade system has been developed using first law of thermodynamics. The derived equations are given below;

The capacity of the evaporator of LTC is defined as

$$Q_E = \dot{m}_L(h_1 - h_4) \quad (1)$$

Compressor power consumption for HTC is given a:

$$W_H=\dot{m}_H(h_6-h_5) \qquad (2)$$

Similarly, compressor power consumption for LTC is

$$W_L=\dot{m}_L(h_2-h_1) \qquad (3)$$

The rate of heat transfer in the cascade system is calculated as

$$Q_{CAS}=\dot{m}_H(h_5-h_8) = \dot{m}_L(h_2-h_3) \qquad (4)$$

The mass flow ratio is determined from

$$\dot{m}_H/ \dot{m}_L = (h_2-h_3)/ (h_5-h_8) \qquad (5)$$

The rate of heat rejection by the condenser of HTC:

$$Q_H= \dot{m}_H(h_6-h_7) \qquad (6)$$

And finally, the overall COP of the cascade system is determined by:

$$COP=Q_E / (W_H + W_L) \qquad (7)$$

Environmental analysis

There are two major parameters measuring the trace of refrigerants on the environment which are Global Warming Potential (GWP) and Ozone Depletion Potential (ODP). Carbon dioxide, has zero ODP and it is used as the base refrigerant for measuring GWP which is equal to 1. One kg of R404A has a GWP of 3800 and one kg of R290 has a GWP of 3. In addition, ODP value is zero for NH_3, R290 and R404A. These values showed that true selection of environmentally friendly refrigerant is crucial to reduce the harmful effects of them on the environment and to decrease contribution to the global warming. Due to the high GWP of R404A it should be totally phased out by 2020 in developing countries (Montreal Protocol) and its amendments from the United Nations Environment Program (UNEP, 1987).

In the present study, two fully and one partially natural refrigerant cases have been studied. In the first fully natural refrigeration solution case, CO_2 is utilized as the refrigerant of the low temperature cycle of a cascade system and ammonia is the working fluid of the high temperature cycle. Using ammonia in low temperature cycle is not proposed since below -35 °C, it has a vapor pressure lower than atmospheric pressure which may cause air leakage into the system besides it is a toxic and flammable refrigerant.

Propane/CO_2 pair is the second fully natural refrigeration solution. Propane has excellent thermodynamic properties, similar to those of ammonia. It is cheap and universally available. The major advantage of selecting propane as the refrigerant over ammonia is that propane is non-toxic. However, its highly flammability feature needs a serious concern and hence safe design and operating practice is of extreme importance.

The partially natural refrigerant cascade system uses the CO_2 as the refrigerant of the low temperature cycle and the synthetic R404A as refrigerant of the high temperature cycle. Currently, CO_2/R404A pair is used more commonly in commercial and industrial refrigeration applications.

Results and discussion

In order to realize an energy efficient and environmentally friendly refrigeration system, CO_2/R404A, CO_2/NH_3 and CO_2/R290 pairs of refrigerants are examined. First two proposals represent fully natural refrigerant solution however the last option corresponds to partial use of natural refrigerants.

The performance and mass flow ratio of the three different cascade systems (CO_2/R404A, CO_2/NH_3 and CO_2/R290) are computed and results are plotted for different operating conditions. These conditions are chosen to examine the effect of the evaporation temperature of cascade condenser ($T_{CAS,E}$), the condensing temperature of high temperature cycle (T_C) and evaporating temperature of low temperature cycle (T_E) on the COP of the system and the mass flow ratio of two cycles.

- **Effect of the evaporation temperature of cascade condenser**

In this case study the evaporation temperature of cascade condenser ($T_{CAS,E}$) was varied between -30ºC and 5ºC by keeping the other operating parameters constant such as condensing temperature of high temperature cycle (T_C =40ºC), evaporating temperature of low temperature cycle (T_E=-50ºC), temperature difference in cascade condenser (ΔT_{CAS}=5ºC). The degree of subcooling and superheat is assumed to be 0ºC in the two stage cascade system.

In Figures 2 and 3, the effect of $T_{CAS,E}$ on both the COP and the mass flow ratio are displayed for the cascade system to select the right refrigerant pair. Figure 2 depicts variation of system COP for NH_3, R290 and R404A in the high temperature cycle with CO_2 in the low temperature cycle. As can be seen from Figure 2, the maximum COP of the system for the given conditions is highest for NH_3 and lowest for R404A. The ratio of mass flow of the refrigerants (NH_3, R290) in the high temperature cycle to that of CO_2 in the low temperature cycle is also compared in Figure 3. The use of R404A in the high temperature cycle requires the highest mass flow ratio ranging from 3.9 to 3.2, whereas using NH_3 requires the lowest mass flow ratio (from 0.34 to 0.32) due to its high latent heat of vaporization. In addition, the mass flow ratio of R290 is calculated between 1.5 and 1.3.

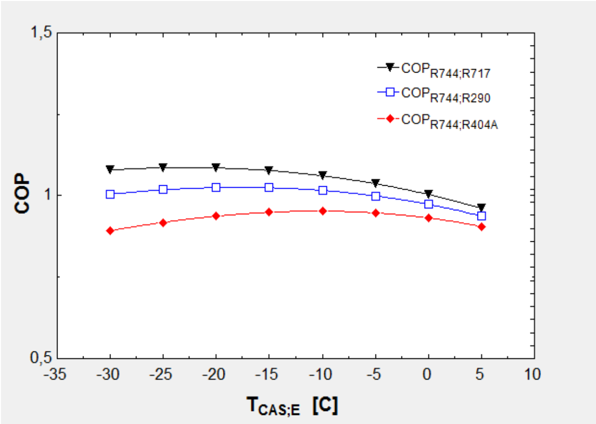

Figure 2. Effect of cascade evaporating temperature ($T_{CAS,E}$) on the performance of cascade systems

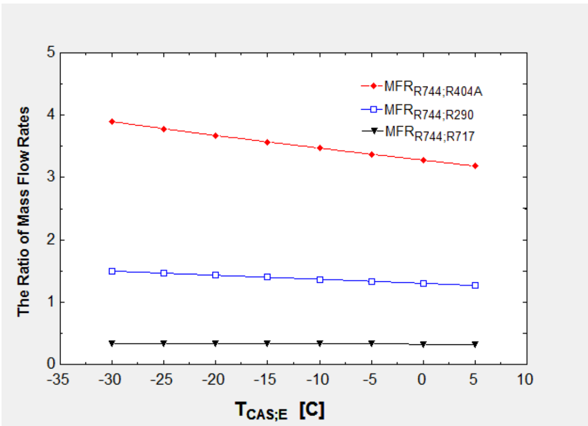

Figure 3. Effect of cascade evaporating temperature ($T_{CAS,E}$) on the ratio of HT to LT mass flow rates

- **Effect of condensing temperature of high temperature cycle**

The condensation temperature (T_C) of high temperature cycle is varied between 25ºC to 45ºC in this case. The evaporation temperature, T_E, for the low temperature cycles and the cascade evaporation temperatures, $T_{CAS,E}$, are chosen to be -50ºC and -20ºC, respectively. In all pairs of refrigerant cycles, the temperature difference in cascade heat exchanger, $\Delta T_{CAS,}$ is assumed to be constant of 5ºC. Furthermore the degree of subcooling and superheat are kept constant of 0ºC.

Figure 4 and 5 depict the variation of COP and mass flow ratio for the change in condensation temperature, T_C, from 25ºC to 45ºC. Increasing the HTC condensing temperatures (T_C), and keeping the $T_{CAS,E}$ and T_E constant affects the performance of the cascade system adversely, as shown in Figure 4. Increasing the condensing temperature reduces to COPs for all pairs of refrigerant cycles. However, in Figure 5, it is observed that increasing of T_C results in increase in mass flow ratio from 0.31 to 0.34 for NH_3, from 1.2 to 1.5 for R290 and from 3.0 to 4.1 for R404A cases.

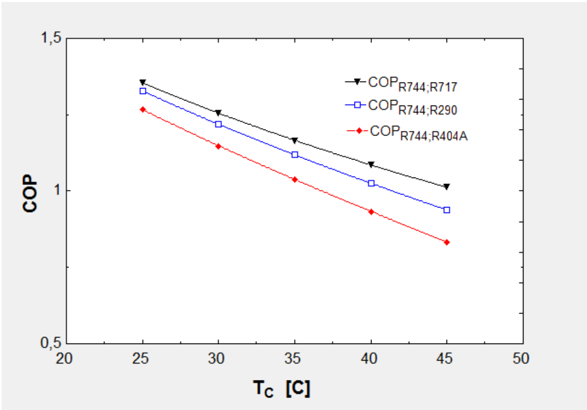

Figure 4. Effect of condensation temperature (T_C) on the performance of different cascade systems

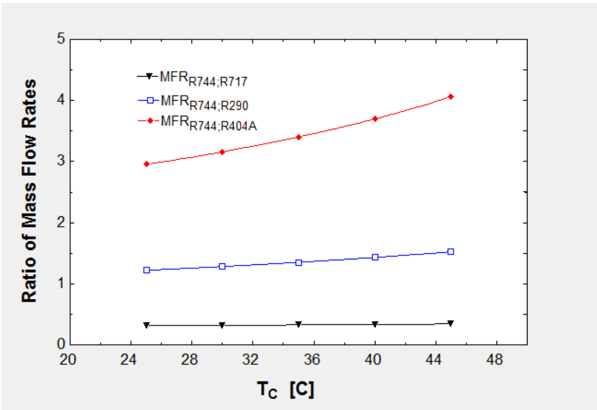

Figure .5 Effect of condensation temperature (T_C) on the ratio of HTC to LTC mass flow rates

- **Effect of evaporation temperature of low temperature cycle**

The evaporation temperature of low temperature cycles (T_E) has varied between -50°C to -25°C in this case studies. The condensation temperature for the high temperature cycles, T_C, and cascade evaporation temperatures, $T_{CAS,E}$, are chosen to be 40°C and -20°C, respectively. In all pairs of refrigerant cycles, the temperature difference in cascade heat exchanger, ΔT_{CAS}, is assumed to be constant of 5°C. In addition, the degree of subcooling and superheat are kept constant to be 0°C.

Figure 6 and 7 illustrate the variation of COP and mass flow ratio for the change in evaporation temperature, T_E, from -50°C to -25°C. As shown in Figure 6, increasing the evaporating temperature rises to COPs for all pairs of refrigerant cycles. However, in Figure 7, it is observed that increasing of T_E resulted in a decrease in mass flow ratio of the CO_2/R404A, CO_2/NH_3 and CO_2/R290 systems.

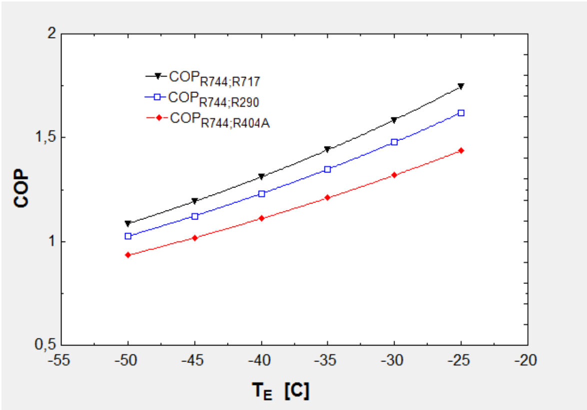

Figure 6. Effect of evaporation temperature (T_E) on the performance of different cascade systems

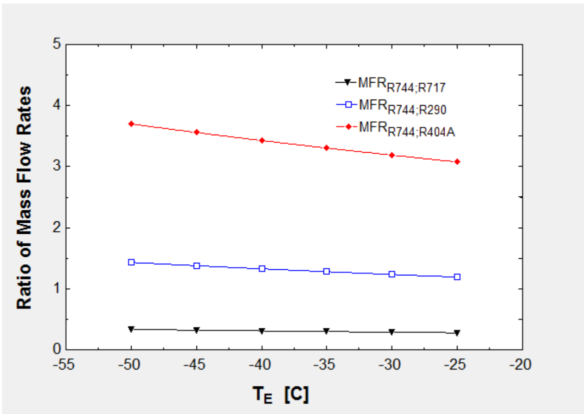

Figure 7. Effect of evaporation temperature (T_E) on the ratio of HT to LT mass flow rates

- **Effect of degree of superheat and subcooling in high temperature cycle**

Superheating case study, the condensation temperature of the high temperature cycles, T_C, the evaporation temperature of the low temperature cycles, T_E, and cascade evaporation temperatures, $T_{CAS,E}$, are chosen to be 40ºC, -50ºC, and -20ºC, respectively. The temperature difference in cascade heat exchanger, ΔT_{CAS}, and the subcooling degree, ΔT_{sub}, are assumed to be constant at 5ºC and 0ºC, respectively.

In Figure 8, degree of superheat (ΔT_{sup}) in HT cycles such as NH_3, R290 and R404A cycles is varied from 0ºC to 20ºC. In addition, degree of superheat and subcooling in LT cycle (CO_2 cycle) are held constant to be

0ºC. An increase of superheat degree from 0 to 20ºC reduced the COP of the CO_2/NH_3 cycle. However the rising of superheat degree resulted in an increase in COP of the both CO_2/R290 and CO_2/R404A systems.

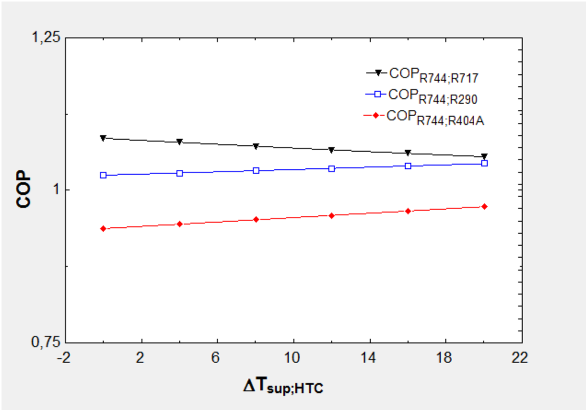

Figure 8. Superheating effect on COP for HTCs

Subcooling case study, the subcooling degree of high temperature cycles (ΔT_{sub}) is changed between 0ºC to 10ºC. The condensation temperature of the high temperature cycles, T_C, the evaporation temperature of the low temperature cycles, T_E, and cascade evaporation temperatures, $T_{CAS,E}$, are chosen to be 40ºC, -50ºC, and -20ºC, respectively. The temperature difference in cascade heat exchanger, $\Delta T_{CAS,}$ and the subcooling degree, $\Delta T_{sub,}$ are assumed to be constant at 5ºC and 0ºC, respectively. In Figure 9, it is observed that increasing the level of subcooling increases the COP for all refrigerant pair cases.

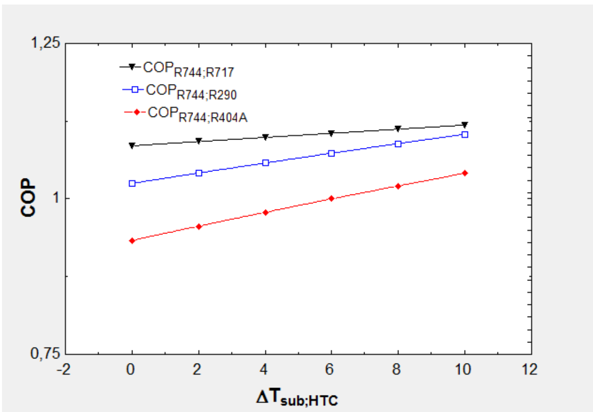

Figure 9. Subcooling effect on COP for HTCs

- **The effect of the cascade refrigerant pairs to the environment**

In this part of the study, the effect of using different the cascade refrigerant pairs on the system performance and the environment has been investigated. The condensation temperature of the high temperature cycles, T_C, the evaporation temperature of the low temperature cycles, T_E, and cascade evaporation temperatures, $T_{CAS,E}$, are chosen to be 40ºC, -40ºC, and -20ºC, respectively. In all pairs of refrigerant cycles, the temperature difference in cascade heat exchanger, $\Delta T_{CAS,}$ is assumed to be constant of 5ºC. The degree of subcooling and superheat are kept constant to be 0ºC. In addition, the evaporation capacity of the evaporators, Q_{EVAP}, is chosen to be 6 kW.

The calculated performances and total refrigerant charge requirements of the different refrigerant pairs are given in Table 1. In addition, GWPs of the three systems (CO_2/NH_3, CO_2/290 and CO_2/R404A), have been examined for the leakage of the whole refrigerant in the cycle to the atmosphere. According to the Table 1 the CO_2/R290 system has a total value of GWP of 15 and the CO_2/R404A system has 45600 according to each refrigerant charge pair. As can be noted, the difference between the CO_2/R404A system and the CO_2/R290 system as calculated to be 45585.

It is found that the cascade refrigerant pair of CO_2/NH_3 results in the highest COP value and the best environmental performance as compared to other refrigerant pairs. It is also observed that the COP of R404A is lower compared to other refrigerants, while that of NH_3 is better compared to R290.

Table 1. Mass flow rates of the refrigerants used and COPs in the pairs of cascade system

Refrigerant pair	**CO_2/NH_3**	**CO_2/R290**	**CO_2/R404A**
Total refrigerant charge (kg)	$m_{CO2} = 25$ $m_{NH3} = 6.5$	$m_{CO2} = 25$ $m_{R290} = 5$	$m_{CO2} = 25$ $m_{R404A} = 12$
GWP	$GWP_{CO2} = 1$ $GWP_{NH3} = 0$	$GWP_{CO2} = 1$ $GWP_{R290} = 15$	$GWP_{CO2} = 1$ $GWP_{R404A} = 45600$
COP	1.3	1.2	1.1

Conclusion

In this study, CO_2/NH_3, CO_2/290 and CO_2/R404A pairs of refrigerants are compared in order to realize an energy efficient and environmentally friendly refrigeration system. For the studied system, the cascade refrigerant pair of CO_2/NH_3 results in the highest COP value and the best environmental performance as compared to other refrigerant pairs. It is also found that the COP of R404A is lower compared to other refrigerants, while that of NH_3 is better compared to R290.

Furthermore, the COP and the mass flow ratio of the refrigerant pair for a cascade system have been investigated for three different cases such as CO_2/NH_3, CO_2/290 and CO_2/R404A. These systems are parametrically analyzed leading to the following conclusions:

- Increasing the HTC condensing temperature, T_C, and keeping the $T_{CAS,E}$ and T_E constant reduces to COPs for all pairs of refrigerant cycles. However, it is observed that increasing of T_C results in increase in mass flow ratio for NH_3, R290 and R404A cases.
- The use of R404A in the high temperature cycle requires the highest mass flow ratio, whereas using NH_3 requires the lowest mass flow ratio due to its high latent heat of vaporization.
- Increasing the evaporating temperature, T_E, rises to COPs for all pairs of refrigerant cycles. However, it is observed that increasing T_E resulted in a decrease in mass flow ratio of the CO_2/R404A, CO_2/NH_3 and CO_2/R290 systems
- It is observed that increasing the level of subcooling increases the COP for all refrigerant pair cases.
- An increase of superheat degree reduced the COP of the CO_2/NH_3 cycle. However the rising of superheat degree resulted in an increase in COP of the both CO_2/290 and CO_2/R404A systems.

Nomenclature

CO_2 (R744)	carbon dioxide
COP	coefficient of performance (dimensionless)
GWP	global warming potential
h	specific enthalpy ($kJ.kg^{-1}$)
HTC	high temperature cycle
LTC	low temperature cycle
m	mass (kg)
$\dot{m}$	mass flow rate ($kg\ s^{-1}$)
MFR	mass flow rate ratio (dimensionless)
NH_3 (R717)	ammonia
ODP	ozone depletion potential
$\dot{Q}$	heat transfer rate (kW)
R290	propane
T	temperature (°C or K)
$\dot{W}$	power (kW)

Greek symbols

Δ	difference

Subscripts

C	condenser
CAS	cascade
E	evaporator
H	high temperature cycle
L	low temperature cycle
sub	subcooling
sup	superheating

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7

Removal of Pb (II) Ion From Aqueous Solution by Adsorption Process onto Paper Mill Sludge: Isotherm and Kinetics

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Abstract

The various experimental parameters such as initial pH of solution, adsorbent dosage, initial concentration of solution, temperature and contact time were investigated for adsorption process of Pb (II) ion onto paper mill sludge (PMS). Results showed that the adsorption capacity was decreased depending on increase in temperature. The pseudo-second order kinetic model was best described the kinetic data. When the experimental data were applied to Langmuir, Freundlich and Dubinin-Redushkevich (D-R) isotherm models, the Langmuir was determined as the most suitable isotherm from among these isotherm models. Furthermore, the mechanism of adsorption process has ion-exchange character since the values of sorption energy were calculated in the range of 14.43-10.78 kJ/mol for all temperatures. The calculated negative values of thermodynamic parameters such as enthalpy (ΔH^o) and free energy (ΔG^o) were revealed the process to be exothermic and spontaneous in nature.

Keywords: Adsorption, Paper Mill Sludge, Pb (II) ion, Isotherm, Kinetic

Introduction

Lead metal is one of the toxic heavy metals may cause the environmental pollution and adversely affects the health of human and many biological species on environment even at low concentrations (Ong, Toorisaka, Hirata, & Hano, 2013). Lead is discharged from different industries such as metallurgical, battery, mining, paint and dyes at high concentrations (Soetaredjo, Kurniawan, Ki, & Ismadji, 2013). It is essential to reduce the permissible concentration limit of wastewater containing Pb (II) ion by using various methods, before Pb (II) ions are discharged (Rao, Khan, & Rehman, 2011). The processes such as membrane filtration (Rivas & Palencia, 2011), adsorption (Yargıç, Şahin, Özbay, & Önal, 2015), ion exchange (Abdel-Aziz, Nirdosh, & Sedahmed, 2013) and precipitation (Lovell, Nancy, ShaKayla, & Kayla, 2013) are commonly used for the removal of heavy metals from aqueous solution. Among the processes, adsorption is the most preferred process because it is applicable and economical process (Singh & Kaushal, 2013). In recent years, agricultural and industrial waste materials such as peanut shell, tomato waste, coconut shell and rice bran were used as low cost adsorbents (Singha & Das, 2013; Yargıç et al., 2015).

Paper mill sludge (PMS) produced by the paper industry was used as adsorbent in this study. The effect of initial pH of solution, adsorbent dosage, initial concentration of solution, temperature and contact time on adsorption of Pb (II) ion onto PMS from aqueous solution was investigated in the batch adsorption experiments. The results obtained from adsorption experiments were applied to the pseudo-first order, the pseudo-second order and intra-particle diffusion kinetic models. The adsorption data were analyzed using Langmuir (Langmuir, 1918), Freundlich (Freundlich, 1906) and Dubinin-Radushkevich (D-R) (Dubinin & Radushkevich, 1947) isotherm models. Thermodynamic parameters such as ΔH^o, ΔG^o and ΔS^o calculated by using the most suitable isotherm for adsorption process. The experiments were carried out in triplicate for reliability, repeatability of results.

Materials and Method

PMS provided from OYKA paper industry in Zonguldak/Turkey was air-dried in the laboratory, crushed and sieved to obtain desired sizes (<100 mesh). The stock solution of Pb (II) (0.25 M) was prepared in the concentration of 0.25 M by dissolving amount of 95.25 g salt of $Pb(CH_3COOH)_2.3H_2O$. All solutions in various concentrations (5, 10, 15, 20, 25 mM) were prepared by diluting with deionized water of 0.25 M stock solution.

The experiments were conducted in 300 mL erlenmayer in an orbital shaker with adjustable temperature and agitation speed (Zhcheng ZHWY-200D). Initial pH values of Pb (II) solutions were measured. After PMS was added to prepared solutions in erlenmayer flasks, the mixtures were agitated under prescribed temperature and time at 200 rpm. The mixture was filtered through the filter paper (Double Rings-203) and pH measurement (Metler Delta 350) was performed in the filtrate. The residual concentration of Pb (II) ion in supernatant was analyzed by Atomic Absorption Spectrophotometer (Perkin Elmer AAnalyst-400).

Analytical Technique

The percentage of adsorbed Pb (II) ion was calculated from the expression;

$$\text{Adsorption yield (\%)} = (C_o - C_s) \times \frac{100}{C_o} \quad (1)$$

The amount of retained Pb (II) ion in the adsorbent phase was expressed as;

$$q = \frac{(C_o - C_s) \times V}{m} \tag{2}$$

C_o and C_s (mM) are the initial and final concentration of Pb (II) solution, respectively. q (mg/g) is the amount of adsorbed lead ion by the adsorbent mass per unit, V (L) is the volume of solution and m (g) is the mass of adsorbent (Esmaeli et al., 2013).

Results and Discussion

To investigate the effect of adsorbent dosage, PMS was added to 200 mL of Pb (II) solution (5 mM) by changing adsorbent dosages from 0.5 to 50 g/L and then agitated through 24 hours. As shown in Figure 1, the adsorption dosage is increased by increasing the removal percentage of Pb (II) ion. For example, while the adsorbent dosage was increased from 0.5 to 5 g/L by increasing removal percentage of Pb (II) ion approximately from 18% to 83%, the removal percentage was reached to maximum value (98%) in 10 g/L adsorbent dosage. After this value, there is no change in the adsorption efficiency. Therefore, the adsorbent dosage was chosen as 10 g/L and the further adsorption experiments were performed in this value.

After determination adsorbent dosage as 10 g/L, further experiments were carried out at the initial pH values of the metal solutions from 2 to 5 during 24 hours, while the other experimental conditions were kept constant. The influence of initial and final pH values of solutions on removal of Pb (II) ion was shown in Figure 2. As seen from Figure 2, the removal of Pb (II) ion was clearly increasing depending upon increasing initial pH value of metal solution and also the highest percentage removal of Pb (II) ion was obtained as 97.6% at pH 5. On the other hand, it was observed that the final pH values of metal solution were higher than initial pH values of solution. This situation may be attributed that the remained aqueous solution has generally basic character because of the adsorbent is containing compounds of calcium and sodium.

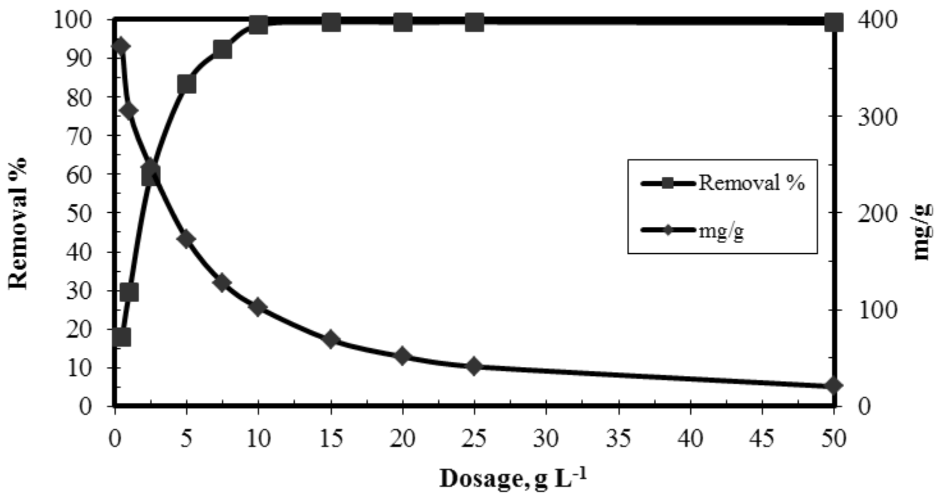

Figure 1. Effect of adsorbent dosage on removal of Pb (II) ion

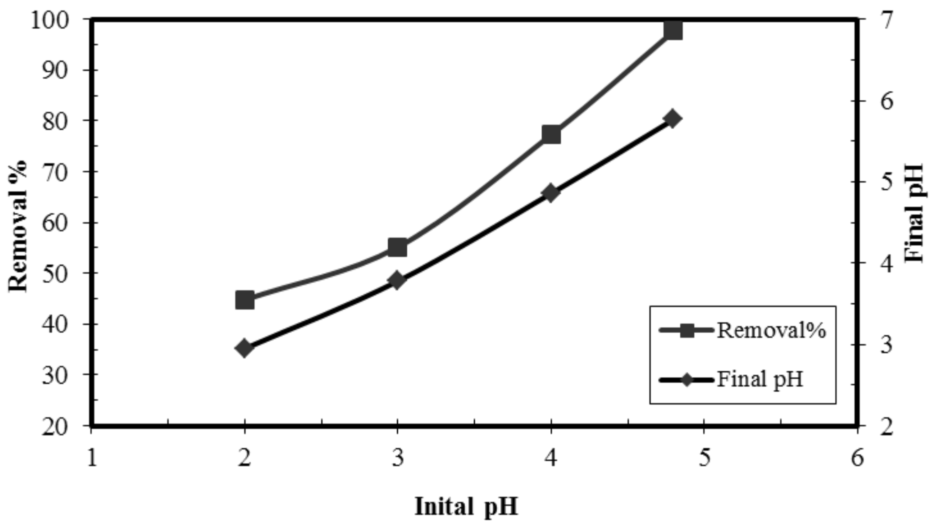

Figure 2. Effect of initial pH on removal of Pb (II) ion

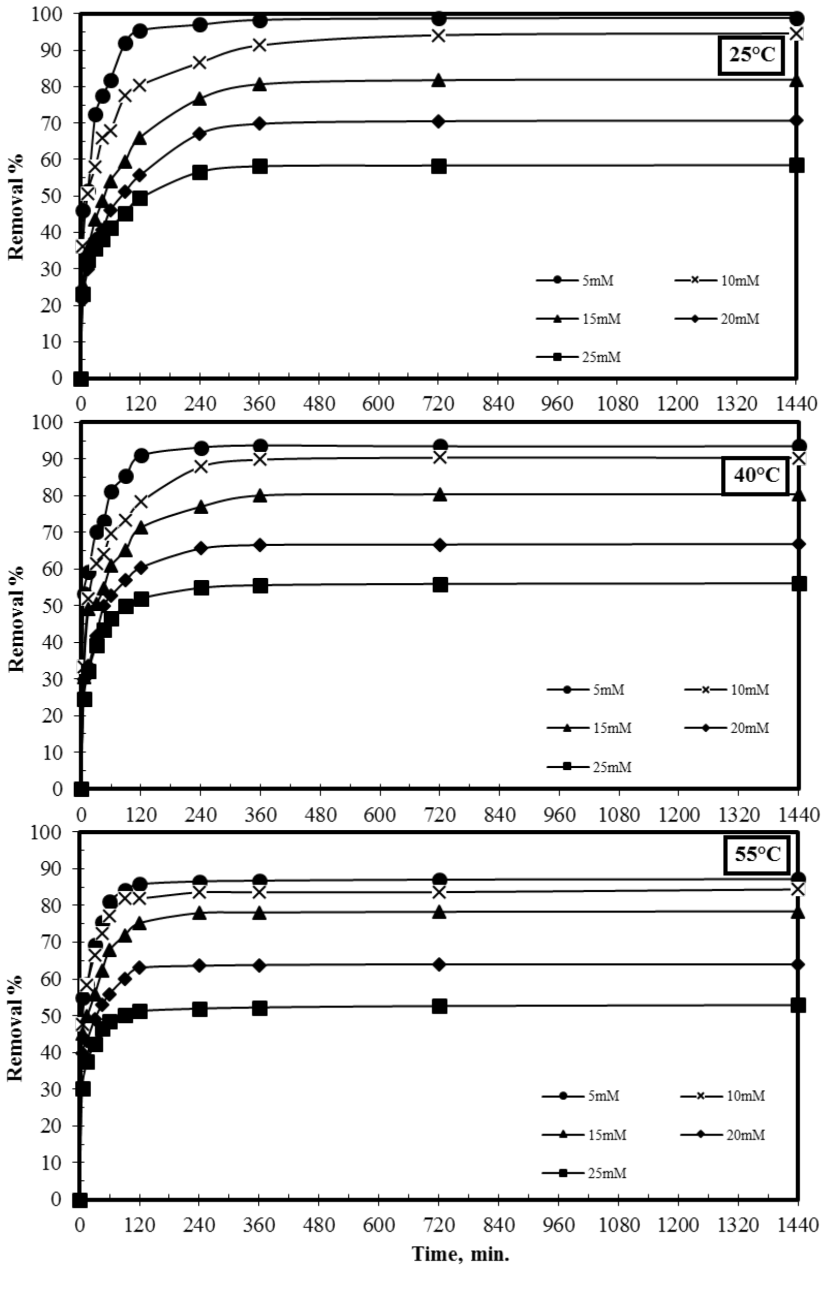

Figure 3. Effect of initial concentration, temperature and contact time on removal of Pb (II) ion

The relationship between the percentage of removal Pb (II) ion and contact time was seen in Figure 3. According to Figure 3, while adsorption of Pb (II) ion onto PMS was gradually increased until 360 min., it was about constant after equilibrium time and achieved the highest value (98%) for all concentrations. Furthermore, it was clearly observed that the adsorption efficiency of metal ion was decreased by increasing from 25 °C to 55 °C resulting from the reduced surface activity of adsorbent. The highest removal percentage of Pb (II) ion was obtained almost 98.9% in 5 mM initial concentration at 25 °C. At the light of these, it was possible indicated that the adsorption process was the exothermic nature.

To assess the kinetic of adsorption process, experimental data were applied to the equations belong to various kinetic models such as the pseudo-first order (Largergren, 1898), the pseudo-second order (Ho, McKay, Wase, & Forster, 2000) and intra-particle diffusion (Weber & Morris, 1963). According to results in Table 1, it was determined that the best fit model is the pseudo-second order kinetic model due to the highest value of R^2 values for all temperatures and the quite closely values of q_{exp} and $q_{cal.}$. Similar results were obtained by some researchers for adsorption process of Pb (II) ion onto different adsorbents (Gedam, Dongre, & Bansiwal, 2015; Taşar, Kaya, & Özer, 2014).

Table 1. Calculated values of kinetic parameters for pseudo-second order kinetic model

Temperature, °C	C_o (mM)	$q_{exp.}$ mg g^{-1}	$q_{cal.}$ mg g^{-1}	k_2 g mM^{-1} min.$^{-1}$	R^2
25	5	102.5	103.1	0.0011	0.9999
	10	196.1	200.0	0.0003	0.9999
	15	254.6	263.2	0.0001	0.9996
	20	292.9	303.0	0.0001	0.9995
	25	303.0	312.5	0.0002	0.9997
40	5	96.85	97.1	0.0015	0.9999
	10	187.22	188.7	0.0004	0.9998
	15	249.9	256.4	0.0003	0.9998
	20	276.4	277.8	0.0003	0.9999
	25	290.6	294.2	0.0003	1
55	5	90.4	91.0	0.0023	1
	10	174.9	175.4	0.0010	1
	15	243.8	243.9	0.0005	0.9999
	20	265.3	270.3	0.0006	1
	25	274.2	277.8	0.0006	1

The Langmuir isotherm is widely used kinetic model to explain the formation of monolayer on the surface of the adsorbent and homogeneous surface of adsorbent in adsorption process. The linear form of Langmuir equation can be written following as;

$$\frac{C_e}{q_e} = \frac{1}{q_{max} b} + \frac{C_e}{q_{max}} \tag{3}$$

Here C_e, q_e and q_{max} represent the Pb (II) ion concentration of solution at equilibrium time, the adsorption capacity of the adsorbent and maximum adsorption capacity of adsorbent respectively. *b* is the a constant linked to adsorption energy.

The equation of Freundlich isotherm describes the formation on heterogeneous surface of adsorbent and given as following;

$$\ln(q_e) = \ln K_f + \left(\frac{1}{n}\right)\ln C_e \quad (4)$$

where K_f is the Freundlich constant and *1/n* is the adsorption capacity. The values of K_f and *1/n* determined from the intercept and slope from straight line of lnq_e vs. lnC_e.

(D-R) isotherm model based on Polany's potential theory of adsorption mechanism is can be expressed as;

$$\ln q = \ln q_m - \beta\varepsilon^2 \quad (5)$$

where β is a constant related to adsorption energy and ε is the Polanyi potential which is equal to $RTln(1+1/C_e)$, where *R* is the gas constant (kj.mol^{-1}.K^{-1}) and *T* is the absolute temperature (K). β constant (mol^{2}kj^{-2}) and q_m value were calculated from slope and intercept of the plot *lnq* vs. ε^2. Accordingly, the obtained isotherms by applying to Langmuir, Freundlich and D-R kinetic models and initial concentration of Pb (II) ion solution in the range of 5-25 mM were showed in Figure 4.

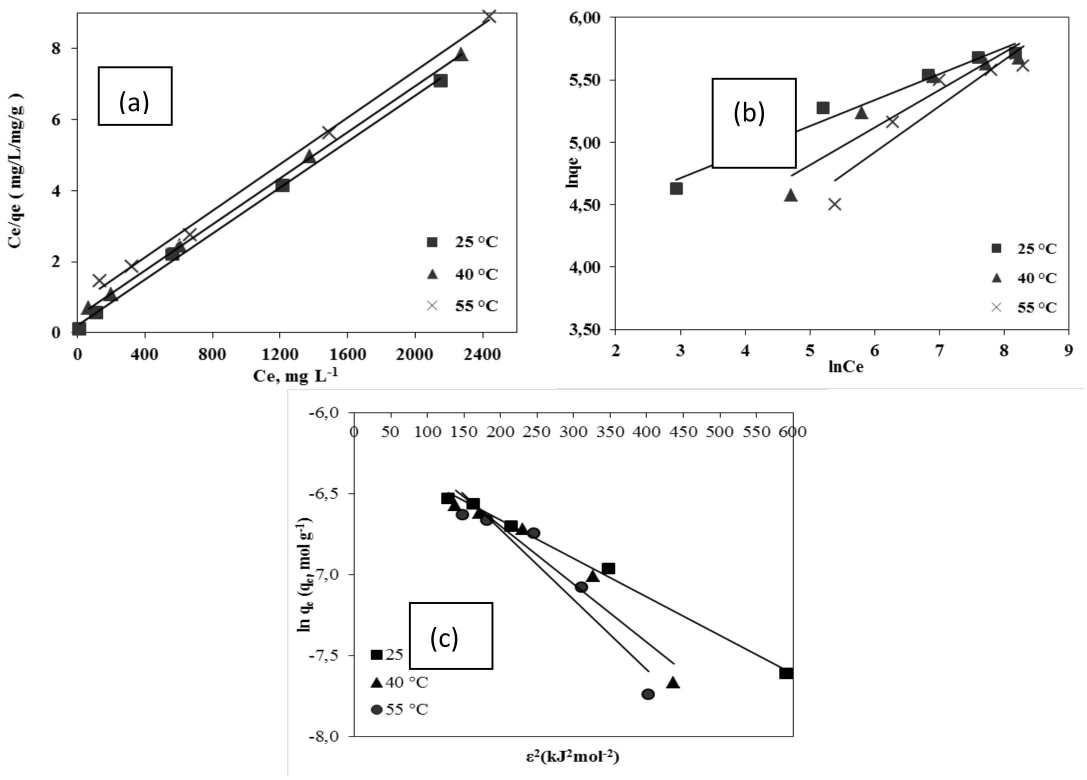

Figure 4. Graphs of (a) Langmuir, (b) Freundlich and (c) D-R isotherms

According to Langmuir isotherm, the state of adsorption process can be evaluate using dimensionless separation factor *(r)* (Khezami & Capart, 2005).

$$r = \frac{1}{1 + bC_0} \tag{6}$$

where r is the dimensionless separation constant, C_o ($mM.L^{-1}$) is the initial metal concentration, b is the Langmuir constant ($L.mM^{-1}$). The value of r is used to indicate the shape of the isotherm. r values indicate the characteristic and feasibility of isotherm to be irreversible $(r=0)$, favourable $(0<r<1)$, linear $(r=1)$ or unfavorable $(r>1)$ (Arslanoglu, Altundogan, & Tumen, 2009).

The calculated values belong to three kinetic models are given in Table 2. The results are showed that the Langmuir isotherm is the most suitable for this process since it has the highest value of R^2. Furthermore, the calculated values of sorption energy from D-R isotherm model were in the range of 14.43-10.78 kJ/mol for all temperatures. Therefore, it can be indicated that the ion-exchange mechanism is dominant for this process. The adsorption capacity of Pb (II) ion was also determined as 310-305 mg/g. The adsorption process is favorable due to the value of dimensionless constant *(r)* is in the range of 0.72-0.98 as shown in Table 3.

Table 2. Calculated parameters and regression coefficients from Langmuir, Freundlich and D-R isotherm models

Temperature, °C	**Langmuir**			**Freundlich**			**D-R**		
	b	q_{max}	R^2	**1/n**	K_f	R^2	q_{max}	**E**	R^2
25	0.0152	309.60	0.998	0.208	65.85	0.971	426.94	14.43	0.994
40	0.0071	307.69	0.999	0.299	32.16	0.895	527.48	11.78	0.937
55	0.0041	304.88	0.996	0.369	17.93	0.859	595.05	10.78	0.905

Tablo 3. Calculated r values for Pb (II) adsorption

Temperature °C	$r = 1/(1+bC_0)$				
	5 mM	**10 mM**	**15 mM**	**20 mM**	**25 mM**
25	0.93	0.87	0.81	0.77	0.72
40	0.97	0.93	0.90	0.88	0.85
55	0.98	0.96	0.94	0.92	0.91

The values of thermodynamic parameters such as entalphy (ΔH^o), free energy (ΔG^o) and entropy (ΔS^o) were calculated by using following equations;

$$\ln\left(\frac{1}{b}\right) = \frac{\Delta G^o}{RT} \tag{7}$$

$$\ln b = \ln b_o - \frac{\Delta H^o}{RT} \tag{8}$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{9}$$

As seen from Table 4, the negative values of ΔG^o and ΔH^o are indicated that the adsorption process is spontaneous nature and exothermic, respectively. The positive change of ΔS^o can be result from increased randomness in the solid/solution interface through adsorption process.

Table 4. Calculated values of thermodynamic parameters

Temperature, ºC	ΔHº (kj/mol)	ΔGº (kj/mol)	ΔSº (kj/mol)
25		-6.74	0.142
40	-35.68	-5.10	0.130
55		-3.84	0.121

Conclusion

The results of present study showed that the paper mill sludge (PMS) may be used as efficient and eco-friendly adsorbent for adsorption of Pb (II) ion from wastewater containing Pb (II) ion at high concentration. The highest removal percentage of Pb (II) ion for adsorption process was obtained at contact time (360 min.), initial of pH=5, temperature (25 ºC), adsorbent dosage (10 g/L) and initial concentration of solution (5 mM) experimental conditions. As a result of different isotherm and kinetic models, the mechanism of adsorption process has ion-exchange character. The adsorption process was spontaneous and exothermic in nature according to the calculated thermodynamic parameters. For further studies, the utilization of PMS and modified PMS as adsorbent can be investigated in adsorption processes of hazardous heavy metals and dyes.

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8

Application of Pervaporation in Environmental Engineering: VFA Separation via Commercial and Manufactured Membranes

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Hatice Yesil
Adile Evren Tugtas

Abstract

Volatile fatty acids (VFAs), which are currently synthesized from fossil fuels, are utilized in various industries. However, scarcity of fossil fuels has generated a new research interest to develop sustainable processes to produce commodity chemicals such as VFAs. Biological synthesis of VFAs through anaerobic fermentation is possible and would decrease the demand for natural resources; however produced VFAs should be separated from fermentation broths. In this study, separation of VFAs via pervaporation, a promising membrane-based technology, was investigated using porous and non-porous membranes and effects of flow rate, feed composition, and membrane type on the separation efficiency were assessed. Optimum flow rate for VFA separation was determined via polytetrafluoroethylene (PTFE) membrane at 55°C at flow rates ranging from 20.8 to 502.8 L/day. Effect of feed composition on separation efficiency was assessed at total VFA concentrations of 5000 mg/L, 10000 mg/L and 20000 mg/L at 35°C using a PTFE membrane. Porous PTFE and non-porous polydimethylsiloxane (PDMS) membranes (non-filled and 2.5% nano-silica filled vinyl terminated (PDMS-vinyl) and hydroxyl terminated (PDMS-OH/PTFE composite)) were used to determine the effect of membrane type on VFA separation. Increasing the feed concentration resulted in significantly increased acid flux and selectivity. Membrane type affected the flux and selectivity of VFAs and the flux of VFAs in different membranes were as follows in increasing order: PDMS-

vinyl < silica-filled PDMS-vinyl < silica-filled PDMS-OH/PTFE composite < PDMS-OH/PTFE composite < PTFE. Whereas, selectivity of VFAs in membranes was as follows in increasing order: PDMS-vinyl < silica-filled PDMS-OH/PTFE composite < silica-filled PDMS-vinyl < PTFE < PDMS-OH/PTFE composite. Results of this study revealed that most efficient VFA separation was observed when PDMS-OH/PTFE composite membranes were used at 35°C with a flow rate of 300 L/d. This study will shed a light to integrated fermentation and membrane-based VFA separation applications, which will hopefully decrease the reliance on fossil-fuels for VFA production.

Keywords: Membrane; pervaporation; recovery; volatile fatty acids

Introduction

Commodity chemicals such as volatile fatty acids (VFAs) are mostly synthesized through fossil fuel-based processes (Eggeman and Verser 2005). However, scarcity of fossil fuel resources has generated a new research interest to develop sustainable processes to produce commodity chemicals such as VFAs (Elliott 2004). Biological synthesis of VFAs through anaerobic digestion of organic-rich wastes is a promising and sustainable technology (Eggeman and Verser 2005). Every year approximately 1.3 billion tons of food with high organic content is wasted globally (Gustavsson et al. 2011). However, organic-rich wastes can be anaerobically fermented to produce commodity chemicals such as VFAs (Tugtas 2014). Anaerobic digestion process is preferentially used to produce biogas and thus energy harvested in the form of methane (Batstone et al. 2002). However, anaerobic digestion processes should not be only considered for biogas production. In addition to biogas production, commodity chemicals such as organic acids (acetic, butyric, lactic acid, etc.) or solvents (ethanol and buthanol etc.) can be produced via anaerobic digestion (Tugtas 2014). VFA production through anaerobic digestion/fermentation should be coupled with a VFA separation technology as accumulated VFAs may inhibit the fermentation process (Arora et al. 2007, Cheng et al. 2010, H.Yesil et al. 2014). VFA separation from various media has been achieved using technologies such as; chemical precipitation (Dionysiou et al. 2000), solvent extraction (Alkaya et al. 2009), adsorption (Garcia 1991), electrodialysis (Wang et al. 2006), distillation (Araromi et al. 2014) and membrane separation (H.Yesil et al. 2014, Qin et al. 2003, Thongsukmak and Sirkar 2007). Pervaporation, a membrane based technology, is a potentially attractive process for the separation of VFAs (Alghezawi et al. 2005). In pervaporation, liquid is in contact with one side of the membrane while vacuum or gas purge is applied on the other side of the membrane facilitating the transfer of components through the membrane (Vane 2005). Operational conditions such as feed concentration, temperature, pressure difference and feed recirculation flowrate may affect the separation efficiency of pervaporation systems (Jiraratananon et al. 2002, Liang et al. 2004). Pervaporative VFA separation have been investigated using various membranes, such as polyaniline (PANI) (Huang et al. 1998), polyvinyl alcohol (PVA) (Isiklan and Sanli 2005), acrylonitrile (Alghezawi et al. 2005), polytetrafluoroethylene (PTFE) (Qin et al. 2003) and polydimethylsiloxane (PDMS) (Bennett et al. 1997). In addition, inorganic fillers such as nano-silica (Sun et al. 2013), zeolite (Zhan et al. 2009), TiO_2 (Yang et al. 2009), and carbon black (Guo et al. 2007) have been integrated to membranes to increase the separation efficiency.

In this study, applicability of pervaporation to environmental engineering field was investigated. Effect of flow rate, VFA concentration, and membrane type on pervaporative separation of VFAs were tested using PTFE, non-filled and filled (hydrophilic nano-silica filled) hydroxyl terminated PDMS-OH/PTFE composite membranes, and non-filled and filled (hydrophilic nano-silica filled) vinyl terminated PDMS membranes.

Materials and Methods

Chemicals

Acetic acid for analysis (No Merck 100063, Millipore Co., Germany); propionic acid for synthesis (No. Merck 800605, Millipore Co., Germany); butyric acid for synthesis (No. Merck 800457, Millipore Co., Germany); valeric acid for analysis (No. Riedel de Haen 27818, Riedel de Haen AG, Germany); caproic acid for analysis (No. Riedel de Haen 60088, Riedel de Haen AG, Germany), hydroxyl terminated PDMS (No. Aldrich 481939, St. Louis, Missouri, USA), n-hexane (No. Acros 197360010, Thermo Fisher Scientific, USA); dibutyltin dilaurate (No. Acros 382690050, Thermo Fisher Scientific, Belgium), tetraethyl orthosilicate (No. Acros 157810010, Thermo Fisher Scientific, Belgium), dicumyl peroxide (No. Merck 8201630250, Merck Millipore Co., USA); hydrophilic silica (No. 1001129031, Sigma-Aldrich Co., USA), Vinyl terminated PDMS (No. Xiameter RBB 2100-30, Dow Corning Co., Midland, Michigan, USA), and concentrated phosphoric acid (H_3PO_4) (Cas No: 7664-38-2, Saf Kimya Co., Turkey).

Membranes

Separation efficiency of VFAs from synthetic VFA mixture was investigated via three different membranes; commercial PTFE membrane (Emflon PTFE, 0.2 µm pore size, Pall Co., Port Washington, New York, USA), vinyl-terminated PDMS membranes (PDMS-vinyl) with and without nano-silica filling, and PTFE supported hydroxyl-terminated PDMS (PDMS-OH/PTFE composite) membranes with and without nano-silica filling. PDMS-vinyl membranes were prepared without a support layer due to their high tensile strength. Vinyl terminated PDMS membranes were fabricated through solvent casting method. PDMS-vinyl polymer was dissolved in hexane of a PDMS/n-hexane ratio of 20% (by weight) using a magnetic stirrer (Heidolph MR Hei-Mix L, Germany) for 12 hours. Hydrophilic nano-silica addition (2.5% by weight of PDMS-vinyl) was carried out at this point for nano-silica filled membranes. The cross-linker dicumyl peroxide was added to the homogenized polymer/hexane mixture with a PDMS/crosslinker ratio of 4%. The polymeric membrane solution was stirred for polymerization reactions for 24 hours. The solution was placed in an ultrasonic water bath (Bandelin, Sonorex DK 156 BP, Germany) at room temperature and 100% power with HF-Frequency 35 kHz was applied to achieve a homogeneous mixture and to prevent possible hexane fuming, which can cause the formation of heterogeneous pores in the membrane. The formed solution was casted on a Teflon plate and the hexane was allowed to completely evaporate at ambient temperature for 24 h. The crosslinking of the membrane was accomplished by gradual heating from ambient temperatures up to 200°C within 7 hours in an oven (Termal G11320SD, Termal Co, Turkey).

Hydroxyl terminated PDMS (PDMS-OH/PTFE composite) membranes were prepared in accordance with mixture casting method. The polymer solution was prepared by dissolving a hydroxyl terminated polydimethylsiloxane (PDMS), cross-linker (tetraethylorthosilicate, TEOS) and catalyst (dibutyltin dilaurate) in hexane. The polymer solution was prepared in constant PDMS/hexane, crosslinker and catalyst ratios of 30% (w/v), 20% (w/v) and 2% (w/w) respectively. Hydrophilic nano-silica addition (2.5% by weight of PDMS-vinyl) was carried out at this point for nano-silica filled membranes. The polymer solution was mixed for 24 hours using a magnetic stirrer (Heidolph MR Hei-Mix L, Germany) in order to homogenize the solution and to initiate polymerization. The polymeric solution was casted on a PTFE membrane with a stainless steel casting blade (Gardco Universal blade applicator, USA) at 254 µm thickness and dried at ambient temperature for 24 hours allowing hexane to evaporate. Subsequently, crosslinking of the membranes were carried out at 100ºC for 24 hours in an oven (Termal G11320SD, Termal Co, Turkey).

Membrane Characterizations

Contact angle and tensile strength analysis were carried out to characterize the membranes. The contact angle of water on membranes were measured through sessile drop method using a tensiometer at ambient temperature (Model: Krüss FM41, A.Krüss Optronic GmbH, Hamburg, Germany). Physical endurance of the manufactured PDMS-vinyl membranes was determined via tensile strength test (Model: Zwick GmBH & Co., Ulm, Germany). Young's modulus of membranes was determined by applying 30 mm/min pulling speed.

Pervaporation Studies

VFA separation assays were conducted with a pervaporation setup (Figure 1). A lab scale two-pieced stainless steel membrane contactor was used. The feed and permeate compartments of the contactor were separated by a membrane with an active surface area of 12.56 cm^2. A 10-16 µm porous glass support was placed in the permeate compartment (Borucam G4, İstanbul, Turkey) to protect the membranes from vacuum. VFA transfer through the membranes were carried out via the use of a vacuum pump (Edward 1.5 Crawley, England) and a vacuum regulator (J-KEM Sceintific-300, USA) creating a constant pressure of 3.0 torrs at permeate side while the feed side was kept under atmospheric pressure (Figure 1). VFA permeated through the membrane was condensed in liquid nitrogen immersed cold traps (KGW Isotherm 17202 KF 29-GL-Z, Karlsruhe, Germany). Samples were taken from the feed and the permeate sides at intervals of two hours. Each assay was conducted for 6 hours. Effect of feed recirculation flow rate on pervaporative VFA separation was assessed using a PTFE membrane and the assays were conducted at 55ºC. Recirculation flow rates at the feed side of the membrane was ranged between 20.8 L/day to 502.8 L/day (20.8 L/d, 102.3 L/d, 212.6 L/d, 376.1 L/d and 502.8 L/d) via a peristaltic pump (Watson Marlow 323, Cornwall, UK).

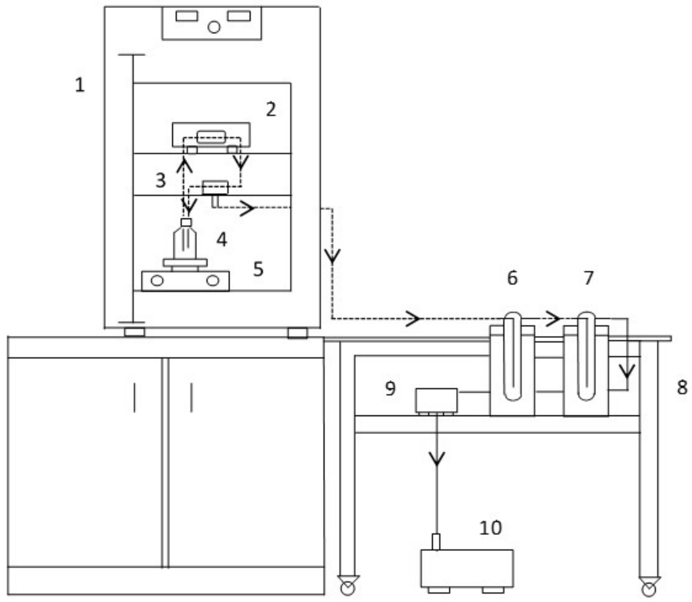

Figure 1. (1) Temperature-controlled cabinet, (2) Peristaltic pump, (3) Laboratory scale membrane contactor, (4) Feed bottle (5) Magnetic stirrer, (6) Inline cold trap, (7) Protector cold trap, (8) Pervaporation table, (9) Vacuum regulator and (10) Vacuum pump.

Feed concentration effect on pervaporative separation was investigated via PTFE membrane under 35ºC, with an optimum flow rate which was determined from flow rate assays. The assays were carried out at 5000 mg/L (1000 mg/L of each acetic, propionic, butyric, valeric and caproic acids), 10000 mg/L (2000 mg/L of each acetic, propionic, butyric, valeric and caproic acids) and 20000 mg/L (4000 mg/L of each acetic, propionic, butyric, valeric and caproic acids) total VFA concentrations. The effect of membrane type on separation efficiency was assessed via non filled PDMS-OH/PTFE composite and PDMS-vinyl polymeric membranes and the effect of filling material on pervaporative separation was examined through including 2.5% hydrophilic nano silica by weight of the polymer (PDMS-OH/PTFE composite or PDMS-vinyl). Both studies were carried out at 35ºC.

Analytical Methods

pH of the feed and permeate samples were measured using a pH meter (Inolab_IDS Multi 9310, WTW GmbH, Germany). Samples were diluted and acidified with 1% phosphoric acid solution and were analysed for their VFA content using a gas chromatography (Model: GC-2014ATF, Shimadzu, Kyoto, Japan) equipped with a flame ionization detector and a capillary GC column (Model: TRB-FFAP 30m x 0.32 mm x 0.50 µm, Teknoroma, Sant Cugat del Velles, Spain). GC was operated under the following conditions: 80ºC column temperature, 260ºC detector temperature, total flow of carrier gas 57.3 mL/min and purge flow 3 mL/min.

Calculations

Membrane selectivity (α) of VFAs was defined by (Thongsukmak and Sirkar 2007);

$$\alpha_{VFA/Water} = \frac{\text{VFA weight fraction in the permeate} / \text{VFA weight fraction in the feed}}{\text{Water weight fraction in the permeate} / \text{Water weight fraction in the feed}} \quad (1)$$

VFA flux (J_{VFA}) or permeation rate through the membrane under pseudo-stationary conditions was calculated by;

$$J = \frac{m}{A.t} \quad (2)$$

where m is the mass of VFA permeated through the membrane (g), A is the membrane surface area (m^2), and t is the time (h).

Reynolds number for various flow rates was calculated by;

$$Re = \frac{uh}{\nu} \quad (3)$$

Where Re is Reynolds number, u is feed velocity on the surface of membrane (m/s); h is the inlet height of feed (m) and υ is the kinematic viscosity (m^2/s) of feed solution (Liang et al. 2004).

Results and Discussion

Membrane Characterization

Contact angle of water on PTFE, filled and non-filled PDMS-vinyl, and filled and non-filled PDMS-OH/PTFE composite membranes were assessed to determine hydrophilic and hydrophobic properties of membranes (Table 1). Among all the membranes studied, PTFE membrane showed the highest hydrophobicity with a contact angle of 143° significantly higher than 90°, demonstrating low water affinity and high hydrophobicity at the surface of the membrane (Li et al. 2010) (Table 1). However, non-filled or silica-filled composite PDMS-OH/PTFE composite membranes or PDMS-vinyl membranes showed hydrophilic properties compared to that of PTFE membranes (Table 1).

Table 1. Contact angles of PTFE, PDMS-Vinyl and PDMS-OH membranes

Membrane	Silica type	Contact Angle (avg±std error)
PTFE	-	143±0.1
Non-filled PDMS-vinyl	-	96.97±0.50
PDMS-vinyl 2.5% filling	Hydrophilic	89.15±0.13
Non-filled PDMS-OH/PTFE composite		108 ± 5.8
PDMS-OH/PTFE composite 2.5% filling	Hydrophilic	104 ± 8.0

The variation in tensile strength of nano-silica filled and non-filled PDMS-vinyl membranes are shown in Table 2. It can be clearly seen that PDMS-vinyl membrane's mechanical strength was greatly enhanced (Table 2).

Table 2. Tensile strength results of vinyl terminated PDMS membranes

Membrane	Silica type	Tensile strength (σ) kg/cm^2	Elasticity Coefficient (E) N/mm^2
Pure	-	1.46±0.36	0.15±0.11
2.5% filling	Hydrophilic	7.78±4.00	0.46±0.38

Effect of feed flow rate

The effect of feed recirculation rate on acid flux and selectivity of mixed VFAs was evaluated with five different flow rates (20.8 L/d, 102.3 L/d, 212.6 L/d, 376.1 L/d and 502.8 L/d) using a PTFE membrane at 55ºC. The experimental results obtained from the pervaporation assays depict that flux and selectivity of VFAs were significantly affected by the flow rate of feed solution (Figure 2). Increasing the flow rate from 20.8 L/d to 502.8 L/d resulted in about two-fold increase in terms of acid flux for all VFAs (Figure 2). Membrane selectivity of acetic, propionic, butyric, valeric and caproic acids, decreased about 24%, 18%, 13%, 9% and 7%, respectively, with the increase in flow rate from 20.8 L/d to 502.8 L/d. The improvement of VFA transfer through the membrane as a result of increased flow rate was due to decrease in boundary layer thickness as a result of increased Reynolds number (Figure 2). In pervaporation process, resistance of boundary layer dominates the overall mass transfer rate of target compound to be separated under laminar flow ($Re<2300$) conditions (Liang et al. 2004, Oliveira et al. 2001). Moreover, the thickness of boundary layer decreases remarkably with the increase of Reynolds number (Liang et al. 2004). Correspondingly, increase in flow rate improved mixture status of feed solution across the membrane surface, causing less boundary layer resistance and higher acid flux under given hydrodynamic conditions. On the other hand, increase of flow rate resulted in an increase of water flux through the membrane. Overall mass transfer resistance for water molecules was probably less due to smaller molecular size of water compared to that of VFAs (Jullok et al. 2015).

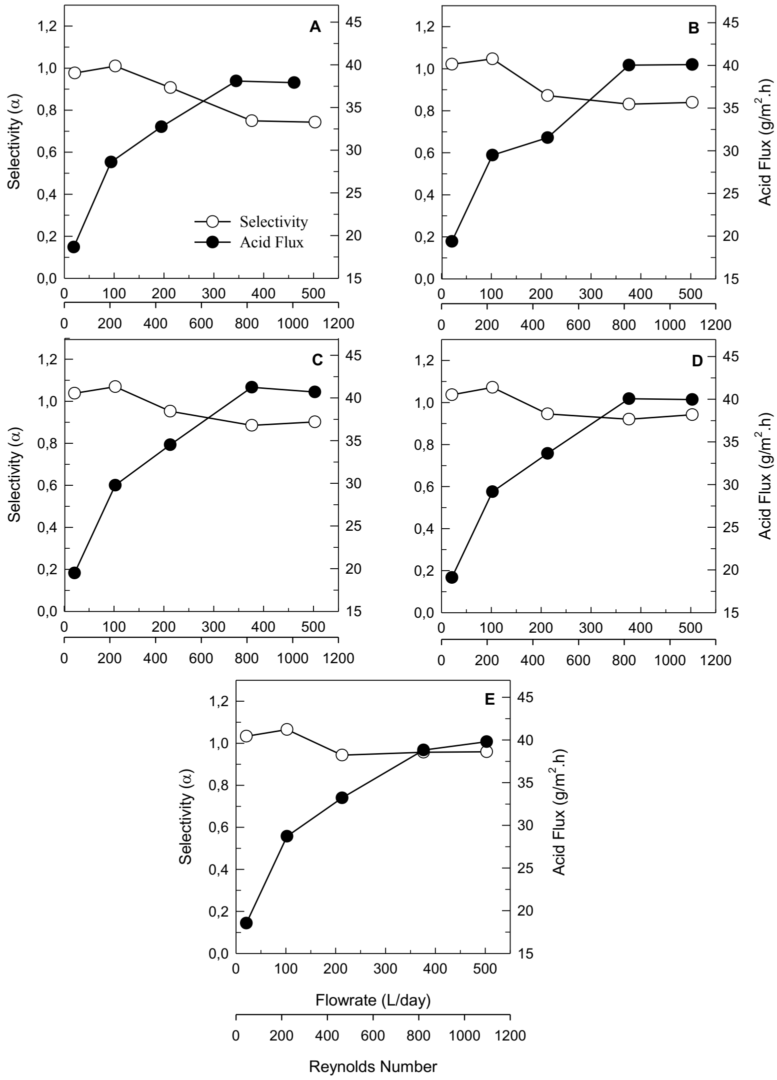

Figure 2. Effect of flowrate on selectivity and acid flux for different acids with PTFE membranes: (A) acetic, (B) propionic, (C) butyric, (D) valeric and (E) caproic acids.

As a consequence, higher water permeation through the membrane was observed with increase of flow rate, which resulted in decrease of VFA selectivity (Figure 2). An optimum flow rate for an efficient pervaporation process was determined considering membrane flux and selectivity together. For all individual VFAs, optimum flux and membrane selectivity was observed at a flow rate of 300 L/d (Figure 2). As a result, other separation assays within this study were conducted by recycling the feed solution with a flow rate of 300 L/d.

Effect of Feed Concentration on VFA Separation

Three synthetic VFA mixtures (Mixture A, B and C) were prepared at total concentrations of 5000 mg/L, 10000 mg/L and 20000 mg/L with 1000 mg/L, 2000 mg/L and 4000 mg/L each of acetic, propionic, butyric, valeric and caproic acids, respectively. Mixture A, B and C were used to investigate concentration effect on separation efficiency of PTFE membranes at 35ºC via pervaporation.

The results of the assay revealed that the flux and selectivity of each VFA increased with increasing feed concentration (Figure 3).

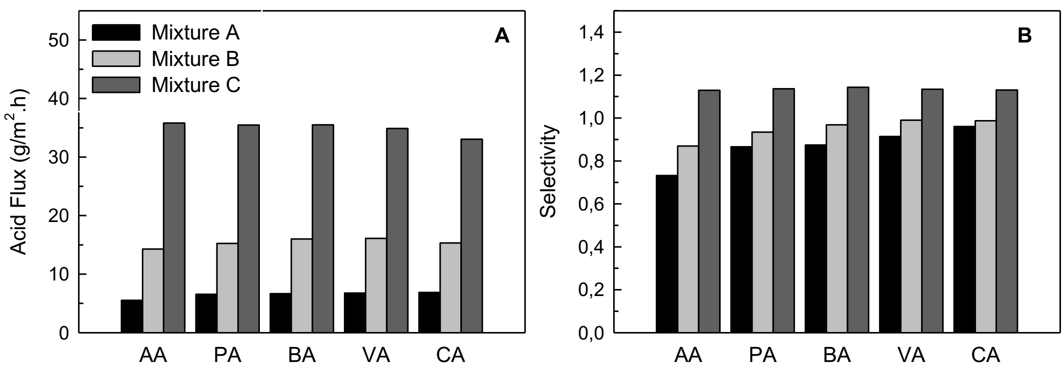

Figure 3. The effect of concentration and feed composition on VFA selectivity and acid flux with PTFE membranes: AA, PA, BA, VA and CA signs are indicating acetic, propionic, butyric, valeric and caproic acids respectively. Mixture A, Mixture B and Mixture C contain 1000 mg/L, 2000 mg/L and 4000 mg/L each of AA, PA, BA, VA and CA, respectively.

Increase of total feed concentration from 5000 mg/L to 10000 mg/L resulted in increase of acid flux for all individual VFAs (Figure 3A). Increase of total feed concentration from 5000 mg/L to 20000 mg/L resulted in seven-fold increase in acid flux and selectivity of VFAs reached above 1.0 (Figure 3). The results indicate that increase in feed concentration results in increase of selectivity and acid flux. Considering the general leachate composition and the results of the assays, feed total concentration was set at 10000 mg/L (2000 mg/L each of acetic, propionic, butyric, valeric and caproic acids) in pervaporation assays using manufactured (PDMS-OH/PTFE composite and PDMS-vinyl) membranes.

Manufactured membranes

Pervaporation of VFAs through non-filled and silica-filled PDMS-OH/PTFE composite and PDMS-vinyl membranes were assessed at 35ºC, 300 L/d feed recirculation flowrate, and 3 torr vacuum. Feed solution was prepared with 2000 mg/L each of acetic, propionic, butyric, valeric and caproic acids. Acetic, propionic, butyric, valeric, and caproic acid selectivities of 2.03, 2.32, 2.75, 3.57, and 4.54, respectively were observed for PDMS-OH/PTFE membranes (Figure 4B). Hydrophilic nano-silica filled PDMS-OH/PTFE composite membrane resulted in dramatic decrease of both selectivity and flux of VFAs compared to that of non-filled PDMS-OH/PTFE membranes (Figure 4). Hong et al., 2011 investigated acetic acid/water separation by pervaporation with silica filled PDMS-OH/PTFE composite membrane under the operational conditions of

30ºC, 624 L/day feed recirculation and 10% acetic acid feed concentration and a decrease of both flux and selectivity was observed upon addition of nano-silica to membrane (Hong et al. 2011). The phenomena was explained as sacrifice of selectivity for increasing permeation flux where addition of nano-silica increased amorphous regions in the membrane therefore more VFA and even more water molecules could go through the membrane (Hong et al. 2011). Non-filled PDMS-vinyl membrane resulted in lower acid flux and selectivitycompare to that of non-filled PDMS-OH/PTFE composite membrane perhaps due to its dense polymeric structure. Addition of nano-silica to PDMS-vinyl membranes resulted in decreased total permeation flux, however the selectivity was increased (Figure 4).

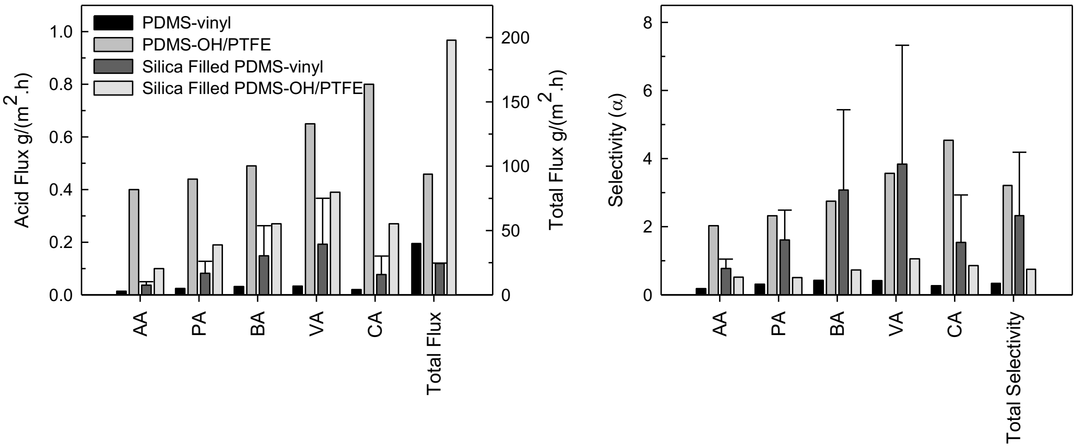

Figure 4. Acid flux (A) and Selectivity (B) for nano-silica filled and non-filled PDMS-vinyl and PDMS-OH/PTFE composite membranes.

Conclusions

In this study, VFA pervaporation efficiencies of PTFE, PDMS-OH/PTFE composite, and PDMS-vinyl membranes were assessed. The results of the study revealed that the recirculation flow rate of 300 L/day was optimum for the separation of VFAs through pervaporation. Increasing the feed concentration resulted in significantly increased acid flux and selectivity. PTFE membranes resulted in highest VFA flux among all the tested membranes. Lowest flux was observed in PDMS-vinyl membranes and the addition of silica slightly enhanced the flux of PDMS-vinyl membranes. Highest selectivity was observed in PDMS-OH/PTFE composite membranes, whereas lowest selectivity was observed in PDMS-vinyl membranes. Addition of silica filling to PDMS-OH/PTFE composite membranes resulted in decreased flux and selectivity. However, addition of silica filling to PDMS-vinyl membranes resulted in increased flux and selectivity.

Acknowledgements

This work was largely supported by The Scientific and Technological Research Council of Turkey (TUBITAK) under Grant number 112Y218. And partially through Marmara University Scientific Research Project Unit (FEN-C-YLP-110316-0102).

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9

Treatment of A Textile Dye in Aqueous Solution Using Fe^0/GAC Micro-Electrolysis System

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Duygu Yamaç

Abstract

In this work, the removal of Deep Red, which is a type of reactive azo dye, from solution was investigated by micro-electrolysis. Micro-electrolysis reactor was filled by iron chip-granular activated carbon (Fe^0/GAC) mixture. In micro-electrolysis experiments the effects of operational parameters such as initial dye concentration (50-200 mg/L), the circulating rate of the solution (9.1-33.1 mL/s), initial pH value of the solution (1-6) and solution conductivity (3-11 mS/cm) were examined. The optimum values of parameters were determined as initial pH of 3, dye concentration of 100 mg/L, feed circulating rate of 9.1 mL/s, and conductivity of 3 mS/cm. Under these conditions 99.5 % Deep Red removal was achieved.

Keywords: Micro-electrolysis, Deep Red, Iron, Granular Activated Carbon, Dye Removal

Introduction

One of the most important pollutants of wastewater in textile industry is dyestuff. Many different types of dyes such as acidic, basic and reactive are used in textile industry. The reactive dyes are preferable for cotton fabrics due to good adhesion properties, and it is known that a significant portion of dye passes through the wastewater due to the hydrolysis side reactions (Pazos et al., 2011). Particularly azo reactive dyes create serious environmental problems. The electrochemical methods such as electrochemical oxidation, electrocoagulation and electro-Fenton have an important place for treatment of the reactive dyes. However, electrical power needs restricts the implementation of these methods on large scale.

Micro-electrolysis (ME) is a low-cost electrochemical method which does not need an external power supply (Zhang et al., 2015). Micro-electrolysis column consists of iron chip and granular activated carbon. When iron (anode) and activated carbon (cathode) are mixed and the solution or wastewater is passed through the column, numerous macroscopic galvanic cells are formed (Yanhe et al., 2016). Compared to electrolysis, rates of electrochemical reactions in micro-electrolysis are very slow due to lack of external electrical supply (Cheng et al., 2007). The half-cell reactions can be represented as follows (Fan et al., 2009):

Anode (oxidation): $2Fe \rightarrow 2Fe^{2+} + 4e^-$ (1)

Cathode (reduction): $4H^+ + 4e^- \rightarrow 4[H] \rightarrow 2H_2$ (Acidic medium) (2)

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ (Acidic medium with oxygen) (3)

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (Neutral to alkaline) (4)

Products released from the galvanic cell reactions include hydroxyl, atomic hydrogen and Fe(II) which have high activities to decompose contaminants (Guo et al., 2013). Also Fe^{2+}, which is evaluated from anodic corrosion, can be oxidized to Fe^{3+} according to following reaction:

$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O$ (5)

Furthermore, organic contaminants can also be removed through coagulation and co-precipitation by the ferrous and ferric hydroxides formed from Fe^{2+} and Fe^{3+} according to the following reactions (Fan et al., 2009):

$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2\downarrow$ (6)

$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3\downarrow + 3H^+$ (7)

In addition, hydrogen peroxide can be generated in the presence of oxygen at acidic conditions (Ren et al., 2011; Lan et al., 2012):

$O_2 (g) + 2H^+ + 2e^- \rightarrow H_2O_2$ (8)

Hydrogen peroxide evaluated according to Eq. 8 can be reacted with Fe^{2+} in solution to generate OH radical known as Fenton's reagent. These radicals are very effective for degrading of organic molecules in wastewater via oxidation (Ying et al., 2012):

$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + {}^{\cdot}OH + OH^-$ (9)

Micro-electrolysis is a low-cost and environmentally-friendly process for the disposal of organic pollutants that cannot be treated with traditional methods due to high chemical stability and low biodegradability (Guo et al., 2013). This method can be used for the different characteristic wastewater such as textile (Yang et al., 2009), petrochemical (Qin ve Gong, 2014), coke (Wen-wu et al., 2012) and polyester (Yang, 2009) industries. By means of micro-electrolysis, the removal of different dye types such as anthraquinone dyes (Qin et al., 2012), acidic dyes (Chen et al, 2013) and azo/diazo reactive dyes (Guo et al., 2013; Yanhe et al., 2016; Karabacakoğlu et al., 2015) from water and wastewater has been studied. In many micro-electrolysis studies, conventional micro-electrolysis column reactors containing Fe and C filling were used (Cheng et al., 2010, Lai et al., 2013), and but in some cases, ozone (Guo et al., 2013) or peroxide (Wang et al., 2016; Chen et al., 2013) was added to wastewater before or after feeding to Fe/C packed reactor.

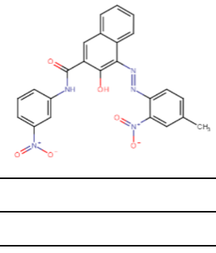
The aim of this study is the treatment of the Deep Red by micro-electrolysis method. In experiments, the effects of operational parameters such as initial dye concentration, the circulating rate of the solution, initial pH value and solution conductivity were investigated.

Material and method

Materials

Waste iron chips were supplied from a metal machining mill (Eskişehir, Turkey). Iron chips and GAC were sieved. Iron chips (0.85 mm<D_p<1 mm) were first treated a 10% NaOH solution for remove the surface grease, and then soaked in a diluted (5%) hydrochloride acid solution for remove oxide layer, and finally cleaned by deionized water. A commercial granular activated carbon (GAC) (Picacarb 830, Pica) was used in the experiments. Before filling the reactor, the GACs (1 mm<D_p<1.4 mm) were cleaned by distilled water, and then soaked in the dye solution of 200 mg/L for 24 h to eliminate the adsorption influence.

Table 1. Some properties of Deep Red

Name	2-Naphthalenecarboxamide, 3-hydroxy-4-((4-methyl-2-nitrophenyl)azo)-N-(3-nitrophenyl)
Molecular Formula	$C_{24}H_{17}N_5O_6$
Molecular Weight	471.429 g/mol
Structure	
EINECS Number	222-643-8
Colour Index	12350

(http1://www.chemicalbook.com/ProductChemicalPropertiesCB8356989_EN.htm)

The reactive azo dye, Deep Red, was provided from a textile factory in Eskişehir, Turkey. The structure and characteristics of dye were illustrated in Table 1. The synthetic wastewater containing the dye was prepared using distilled water. pH and conductivity were adjusted to desirable values using HCl and Na_2SO_4, respectively.

Experimental procedure

The experimental setup consists of a reactor, a peristaltic pump and an air pump (Fig.1). The micro-electrolysis reactor was made of glass. The diameter and length of the reactor were 2 cm and 19.5 cm, respectively.

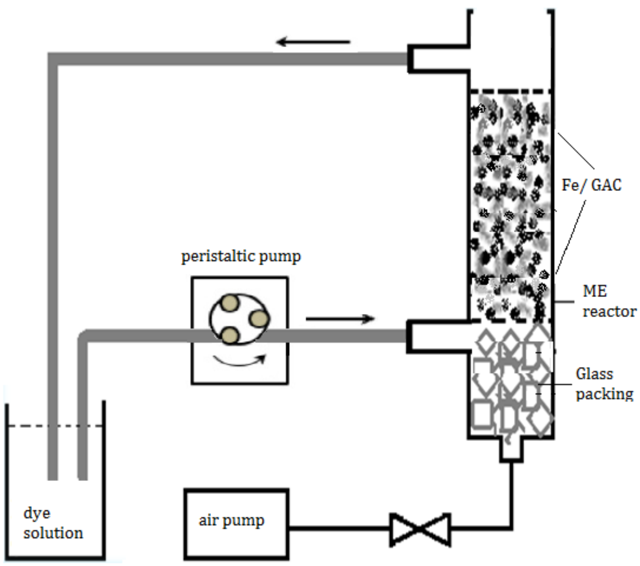


Figure 1. Experimental setup

Iron chips and GAC were mixed together with a volume ratio of 1:1 and then packed to the ME reactor. The height of the packed was 8.5 cm. This ratio of iron to activated carbon is the optimum value determined in many studies (Yanhe et al., 2016; Lai et al., 2012; Chen et al., 2013). The empty bed contact time was around 6 minutes. The dye solution was circulated through the reactor by peristaltic pump, and air was fed into the bottom of the column by air pump. Experiments were carried out in recirculated batch mode. All experimental studies were made with a model solution volume of 200 mL. A sample of 4 mL from dye solution was taken every 15 minutes. The concentration of Deep Red was determined by measuring the absorbance at λ_{max}=519.5 nm with UV spectrophotometer (Aquamate). Dye removal efficiency was calculated according to Eq. (10):

$$Dye\ Removal\ Efficiency\ (\%) = \frac{C_0 - C}{C_0}.100 \quad (10)$$

where C_0 is the initial concentration of dye (mg/L), C is the concentration of dye in time t (mg/L).

Results and discussion

The effects of initial dye concentration (50-200 mg/L), the feed rate (9.1-33.1 mL/s), initial pH value of the solution (1-6) and solution conductivity (3-11 mS/cm) on the removal efficiency of dye were examined.

Effect of time

All the experiments, in which the parameters were examined, were carried out by measuring the change in Deep Red concentration over a certain period of time. Therefore the effect of time on the percentage of dye removal is clearly visible in all figures. There was a sharp increase in the first 15 minutes, and it is observed that the dye removal has changed more slowly especially after 30 minutes in all experiments. The results showed that with the reaction time increasing, the removal efficiency of Deep Red increases. This indicates that the extension of reaction time can effectively improve the degradation efficiency of dye in the ME reactor.

Effect of Deep Red concentration

Fig. 2 shows the variation of the removal efficiency with dye concentration. The removal of Deep Red can reach 80% after 30 min for concentration of 200 mg/L, whereas it is above 90% for low concentrations. Similar results were obtained by Ren et al. (2011). For this reason, it is necessary to increase the amount of column filling for higher removal in a shorter time for higher concentrations. This is more important in continuous micro-electrolysis studies.

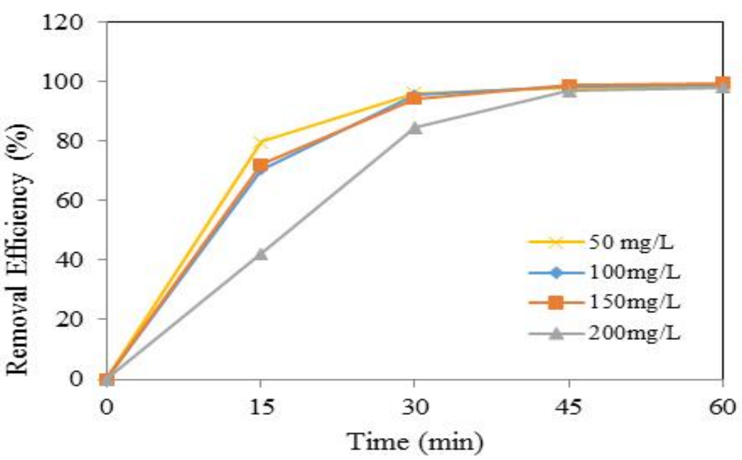


Figure 2.Effect of dye concentration on the removal efficiency (Flow rate: 11.4 mL/s, pH:3).

Effect of initial pH

The most important variable affecting the efficiency in ME studies is pH value of the solution. The pH value of textile wastewaters varies from 4 to 11 depending on the type of dye used. However, microelectrolysis reactions occur under acidic conditions. For this reason, the pH range of the experiments was determined as 1 and 6.35 (original pH of the solution). Fig. 3 shows the effect of pH on the removal efficiency. Removal efficiencies improved with the pH declining from 5 to 3, but decreased slightly when pH changed from 3.0 to 1.0. Therefore, pH was controlled at about 3 in the other experiments. Similar results can be seen in some studies in the literature (Cheng et al., 2010; Huang et al., 2014).

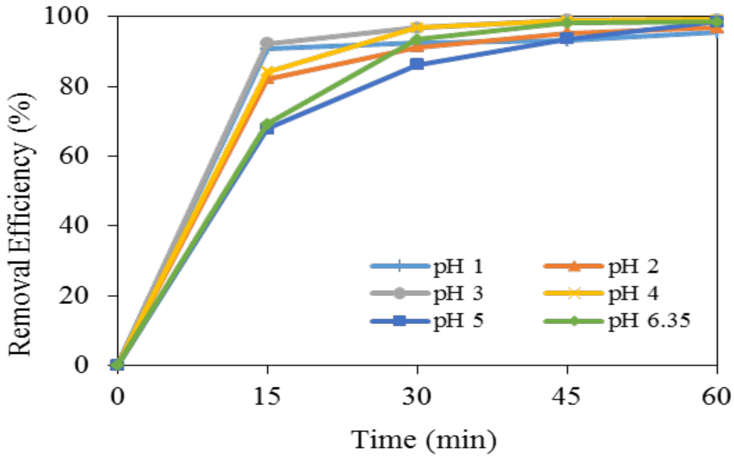


Figure 3. Effect of pH on the removal efficiency (Flow rate: 11.4 mL/s, pH:3, C_o: 100 mg /L)

The pH of wastewater affects the chemical state of pollutants and the molar ratio of Fe(II)/Fe(III) (Wen-wu et al., 2012) and the electrostatic interaction by modifying the surface charge of the GAC (Lai et al., 2013). The electromotive force of the galvanic cell reactions given in Equations 1-4 is very high in the presence of oxygen under acidic conditions. The hydroxyl radical has an extremely high redox potential (E^0 = 2.8 V), and therefore it can react with most pollutants in ambient temperature and pressure. Acidic conditions are also required for the production of .OH radicals. In addition, the increase in H^+ concentration accelerates the corrosion of iron (Li et al., 2011; Chen et al., 2013; Xu et al., 2016). However, large amounts of hydrogen generating under acidic condition inactivate the iron, which inhibits the microscopic galvanic cell reaction. Especially in the case of pH of 2 and 1, the corrosion of the iron accelerated and excess iron hydroxide causes the bed to be clogged. Excess iron hydroxide remaining in the treated solution is another problem. Also, large amounts of Fe^{2+} generating with the stronger acid will disturb the detection of chroma due to color-rendering property (Yanhe et al., 2016).

Effect of solution conductivity

In electrochemical methods such as electrolysis and electrocoagulation, the solution conductivity is considerably effective. In these experiments, the supporting electrolyte of Na_2SO_4 at concentrations ranging from 2.5 to 10 g/L was added to check its effect in the micro-electrolysis process. Studies were performed in four different solution conductivity values to investigate their effects.

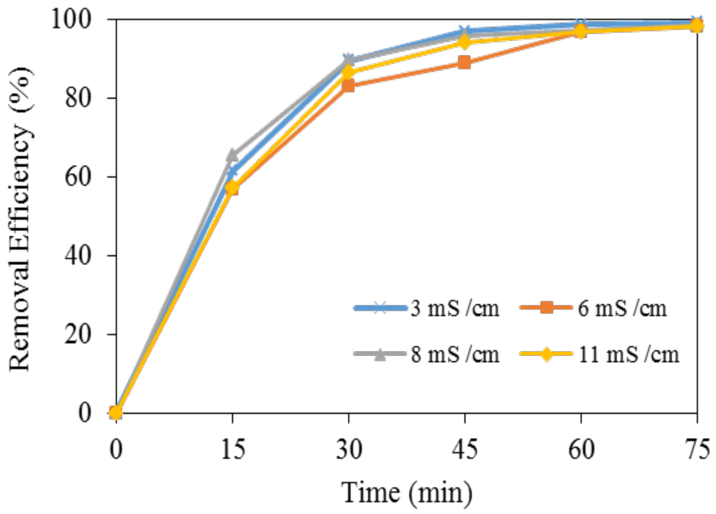


Figure 4. Effect of conductivity on the removal efficiency (Flow rate: 11.4 mL/s, pH:3, C_o: 100 mg /L)

Fig. 4 clearly shows that the conductivity is not effective on the dye removal. At the end of the 75-minute test period for each conductivity value, a recovery of 98% -99% was achieved. The optimum value of conductivity was selected as 3 mS/cm in view of chemical consumption. On the other hand, sodium sulfate was not added in all studies except the experiments where the effect of conductivity was examined, and about 99% removal was achieved. Accordingly, it can be said that the micro-electrolysis process can be performed without the addition of supporting electrolyte.

Effect of circulating rate of solution

The effects of feed circulating rate on the removal efficiency of Deep Red were given in Fig. 5

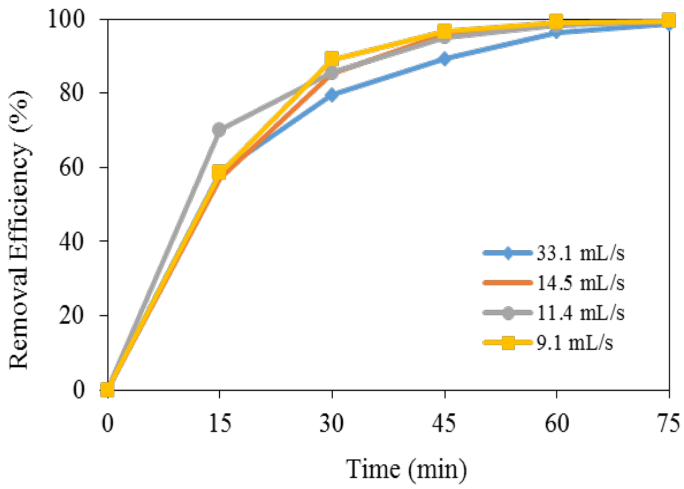


Figure 5. Effect of feed flow rate on the removal efficiency (pH:3, C_o: 100 mg /L)

As shown in Figure, the removal efficiency of dye rises with the decrease of feed flow rate, and the best removal performance was observed at flow rate of 9.1 mL/s. The optimum values of parameters were determined as initial pH of 3, dye concentration of 100 mg/L, feed circulating rate of 9.1 mL/s, and conductivity of 3 mS/cm. Under these conditions 99.5 % Deep Red removal was achieved. The results showed that the process of ME was an efficient and economical method to treat Deep Red solution.

Conclusion

In this study, Deep Red treatment was carried out by micro-electrolysis method using a mixture of iron shavings and activated carbon. The cost of the ME process is determined primarily by the cost of the iron and the active carbon used as the reactor filling. Iron shavings are very cheap because they are supplied from metal processing residues. Activated carbon, the other filling material, can be used for a long time without being regenerated. However, an iron oxide layer is formed on the Fe particles over a long period of use. This layer reduces the catalytic activity and the number of galvanic cells, because it is electrically insulating. Therefore, the bed can be occasionally washed with dilute acid solution to use the ME rector with long-term high yield. In the process of ME electrical energy is consumed for pumping of solution and air. For this reason, it is more economical than the electrochemical processes in which the electric current is directly used as the processing means. As a result, micro-electrolysis method has shown that the reactive dyes can be removed with high efficiency without applying electrical current. However, it is preferable to work with diluted wastewater so that the ME method alone can be sufficient. The effect of the amount of filling can be examined to increase efficiency. In large scale applications, it will be necessary to use the amount of filling material that can provide adequate remediation in a single pass. Also suitable air distributors should be used for effective air flow.

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10

Production of Polyester Composite Material Using Pine Cone Powder as Reinforcement

Duygu Gökdai
Alev Akpınar Borazan

Abstract

Natural fiber reinforced polymer composites have much potential as a progressive material in many industrial applications. Although pine cones have fibril morphology and good mechanical properties they are rarely used as reinforcement in polymer composites. In this study, polymer matrix composites were produced using pine cone waste as reinforcement and polyester as polymer matrix with the casting method. Before mixing the polyester and filler the pine cones were chemically treated to avoid weak coherence between the natural fibers and polymer matrix and to clean their surface and corroborate binding with the polymer. Some mechanical and physical properties of composite materials were analyzed and the composites tested to determine their flexural strength, elastic modulus and hardness. Physical features such as density and water absorption were also investigated. Increasing the ratio of pine cone filler led to an increase in flexural strength values and a decrease of elastic modulus. Chemical treatment applied to pine cones reduced the increasing ratio of flexural strength and also the decreasing ratio of elastic modulus. Increasing the amount of cones reduced the impact strength and was supported by increasing the amount of open porosity. This was because the high amount of pine cone increased both the porosity of the composite and water absorption.

Keywords: Polymer matrix composites, pine cone waste, polyester, mechanical properties

Introduction

Recently; there has been wide interest in the production of natural fiber/particle reinforced polymer composites that have great potential in many application areas like construction, packaging, electronics and automotive industries (Baştürk et al., 2015; Prasad & Rao, 2011; Wei & Gu, 2009). As a result of increasing environmental problems researchers have focused on new sustainable bio-composite materials (Zhan et al., 2011). Polymer based composites have some significant features such as light weight and good mechanical and tribological responses (Gopinath et al., 2014). Several recently conducted studies on this subject are available. Arrakhiz et al. researched the mechanical and thermal properties of clay and pine cone fiber reinforced polypropylene hybrid composite at a total weight percent of 30. The tensile property results indicate that the Young's modulus increased for whole systems reaching a gain of 80%, while tensile strength remained stable with the use of both charges (Arrakhiz et al., 2013). In another study of Arrakhiz et al. fiber–matrix adhesion was assured by both a styrene–(ethylene–butene)–styrene triblock copolymer grafted with maleic anhydride (SEBS-g-MA) and a linear block copolymer based on styrene and butadiene compatibilizer. Results show a clear improvement in mechanical properties from the use of both alkali treated pine cone and pine cone compatibilized with maleic anhydride, with gains of 43% and 49%, respectively in the Young's modulus (Arrakhiz et al., 2012). In the study of Ramesh et al. sisal–jute–glass fiber reinforced polyester composites were developed and their mechanical properties such as tensile strength, flexural strength and impact strength were evaluated. The results indicated that the jute composite material shows maximum tensile strength and can hold the strength up to 229.54 MPa. The maximum impact strength was obtained for the sisal fiber composite and had the value of 18.67 joules (Ramesh et al., 2013). Zhang et al. investigated the mechanical behaviors of unidirectional flax and glass fiber reinforced hybrid composites with the aim of investigating the hybrid effects of the composites made with natural and synthetic fibers. The tensile properties of the hybrid composites were improved with increase of the glass fiber content. They concluded that the fracture toughness and interlaminar shear strength of the hybrid composites were even higher than glass fiber reinforced composites because of the excellent hybrid performance of the hybrid interface (Zhang et al., 2013). Another study of composites with fiber reinforcement was made by Sathishkumar et al. In this study the tensile properties of snake grass fiber were studied and compared with other traditionally available natural fibers. Isophthallic polyester resin was used to prepare the mixed chopped snake grass fiber reinforced composite. The experimental results showed that the volume fraction increases the tensile, flexural strength and modulus of the snake grass fiber reinforced composite (Sathishkumar et al. 2012). Rokbi et al. studied the effect of chemical treatment on the flexure properties of natural fiber-reinforced polyester composite. They used alfa fiber as a reinforcement extracted from the plant Stippa tenacissima from the Hodna Region (Algeria). Alfa fibers were treated with NaOH at 1, 5 and 10% for a period of 0, 24, and 48 h at 28 °C. The experimental results showed that the bending behaviors of composites made from alkali treated fibers were better compared to the untreated fiber composite. For a fiber processing Alfa 10% NaOH for 24h, the flexural strength and flexural modulus improved by 23 MPa to 57MPa and from 1.16 to 3.04 GPa. However, the flexural properties of composites decreased after alkali treatment with 5% NaOH for 48 h (Rokbi et al., 2011). Rout et al. also investigated the influence of fiber treatment on the performance of polyester composites. Hybrid composites containing glass fiber mat (7 wt.%), coir fiber mat (13 wt.%) and polyester resin matrix were prepared. Hybrid composites containing surface modified coir fibers showed significant improvement in flexural strength. Water absorption studies of coir/polyester and hybrid composites showed significant reduction in water absorption because of the surface modifications of coir fibers (Rout et al., 2001). Unlike the study of Rout et al., Gu had different results in a similar study. In the research of Gu brown coir fibers were treated by NaOH solution with concentrations from 2% to 10% separately. Tensile strength of the alkali-treated fibers was measured. A decreased trend of the fiber tensile strength was found with increased NaOH density (Gu, 2009). In this study we aimed to produce polyester composite using pine cone waste as filler. Pine cone is a renewable resource that has great potential for use in many areas. In winter it is generally collected, dried to facilitate seed release, and burned in stoves. Cones are easily accessible making them usable and preferable as reinforcement. Turkey has 54,000 ha of stone pine forests that produce 3,500 tons of pine cone annually (Ayrilmis et al., 2009). In terms of of sustainability, this value has significant importance for evaluating pine cone waste in manufacturing composites that can be used in furniture and some construction materials.

Material and Method

Materials

Polyester resin (Polipol 383-G, Poliya Composite Resins and Polymers Inc., density of 1.076±0.05 g/cm^3) was used as the polymer matrix in all experiments. While methyl ethyl ketone peroxide (MEKP,Butanox™ M-60, AkzoNobel Products) was used as hardener for polyester resins Cobalt 2% solution was used as promoter. Pine cone waste was used as reinforcement. The pine cones were dried in air conditions before mixing with the polymer and they were also chemically treated to avoid weak coherence between the matrix and filler.

Composite Preparation

The polyester matrix was compounded with reinforcement fillings at different ratios by weight (Table 1). A gas pycnometer Micromeritics the AccuPyc II 1340 model (respectively 4.1120±0.0029 g/cm^3 - 1.4493±0.0010 g/cm^3) was used to measure absolute volume and true density of pine cones. Both chemically treated and untreated pine cones were first mixed with polyester resin in the indicated ratios. After compounding was performed using speeds of 500, 1000 and 1500 rpm (Stuart scientific mechanical stirrer), each for a cycle time of five minutes, the mixture was held under vacuum for 5 min. Then accelerator and hardener were added and the final mixture was poured into a mold. Curing conditions for composites were 110 °C, for two hours in an oven (Binder,Germany) and for one day at ambient temperature. The mixture preparation and casting processes are given in Figure 1.

Table 1. Composition of polyester composites

Sample Code	P*** [wt%]	Polyester[wt%]**
PC1	6	94
PC2	9	91
PC3	12	88
PC1ct*	6	94
PC2ct*	9	91
PC3ct*	12	88

** chemically treated composite samples*

*** [wt%]: Weight Percent*

****P: pine cone powder*

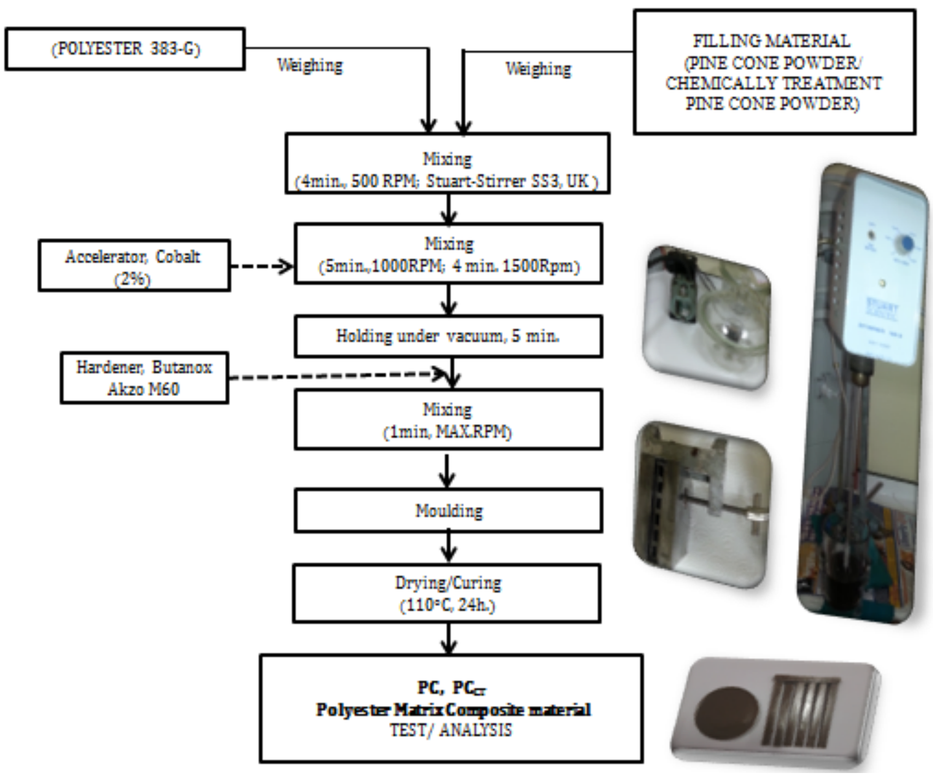

Figure 1. Composite production flowchart

Characterizations

Mechanical Analysis

The mechanical properties of composites were investigated by three point bending tests that were applied at a bending speed of 2 mm/min in a Shimadzu AG-IC Test Machine. The izod impact test was conducted with the DVT CD device, Devotrans Quality Control Test Instruments Ltd., Turkey. Durometer Hardness was used to determine the relative hardness of composite samples. The flexural moduli of the composites were calculated. The cast sizes used in the experimental studies were 10mm x 4 mm x 100 mm. Mechanical properties were calculated according to the following equations by calculating the mean of the three samples.

$$\sigma = (3LP)/(2bd^2) \tag{1}$$

$$E_f = (L^3 m)/(4bd^3) \tag{2}$$

σ : Flexural strength (N/mm^2),
E_f : Flexural modulus (MPa),
L : the support span (mm),
P : the maximum load (N),
b : the width of the composite sample (mm),
d : the thickness of composite sample (mm),
m : the slope of the initial straight line portion of the load displacement curve.

Physical Analysis

Each sample was divided into two pieces after the bending test. These separated samples were dried in an oven at 110°C until they reached a constant weight. Their dry weights were measured at room temperature. They were placed in boiling water to determine the water absorption of composite materials. After boiling for two hours composites were held at room temperature for 24 hours. The suspended weights of the samples were measured in water in a mechanism prepared using the Archimedes density determination kit (WA). The samples were taken out of the water and measured by a balance. The weights of the water-absorbed samples (WD) in the air were recorded. By using the following equations water absorption, bulk density and percentage open porosity values were calculated.

$$A, \% = [(WD - WK) / WK] * 100 \tag{3}$$

$$B = [WK / (WD - WA)] * \rho_{water} \tag{4}$$

$$P, \% = [(WD - WK)/(WD - WA)] * 100 \tag{5}$$

A : Water Absorption,
B : Bulk Density,
P : Open Porosity

Results and Discussion

The experimental results and tests showed that (Figure 2 and Figure 3) hardness value of composite materials decreased for the untreated samples by increasing the pine cone ratio. For chemically treated samples hardness increased with the filler ratio. Increasing the ratio of pine cone filler led to an increase in flexural strength values and a decrease of the elastic modulus. Chemical treatment applied to pine cones reduced the increasing ratio of flexural strength and also the decreasing ratio of elastic modulus. Increasing amounts of cones reduced the impact strength as supported by an increase in the amount of open porosity. This could be due to the fibrous structure of the pine cone, which is clearly visible in the SEM images. Fibrous structure of pine cone led to the connection between the composite layers that were seen to have increased the composite's strength (Baştürk et al., 2015). High amounts of pine cone increased both the porosity of the composite and water absorption (Table 2). This is because of the hydrophilic nature of pine cone in the composites. This can be explained by the fact that pine cone consists of lignin and cellulose and the cellulose has a hydrophilic structure that includes hydroxyl groups. This hydroxyl group easily reacts with the hydrogen bond of water molecules leading to high moisture in the composite (Dan-mallam et al., 2015; Dhakal et al., 2007).

Table 2. Physical and mechanical properties of composite samples

Sample code	Bulk Density (g/cm^3)	Open Porosity (%)	Water Absorption (%)	Izod Impact (J/mm^2)	ShoreD	Flexural Strength (N/mm^2)	Elastic Modulus (GPa)
PC1	1.19	1.86	1.38	5.27	88.00	59.46	5.34
PC2	1.19	1.92	1.56	5.12	87.00	66.328	5.18
PC3	1.19	1.94	1.64	5.02	86.00	71.68	4.66
PC1ct	1.18	2.06	1.75	5.14	85.00	53.59	5.72
PC2 ct	1.17	2.25	1.90	4.96	85.67	56.48	5.62
PC3 ct	1.16	2.44	2.25	4.64	86.67	64.65	5.08

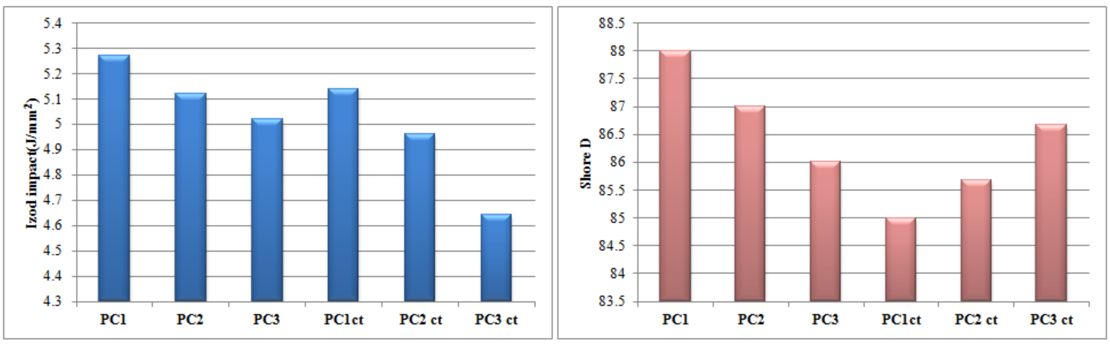

Figure 2. Izod impact and hardness results of the composite samples

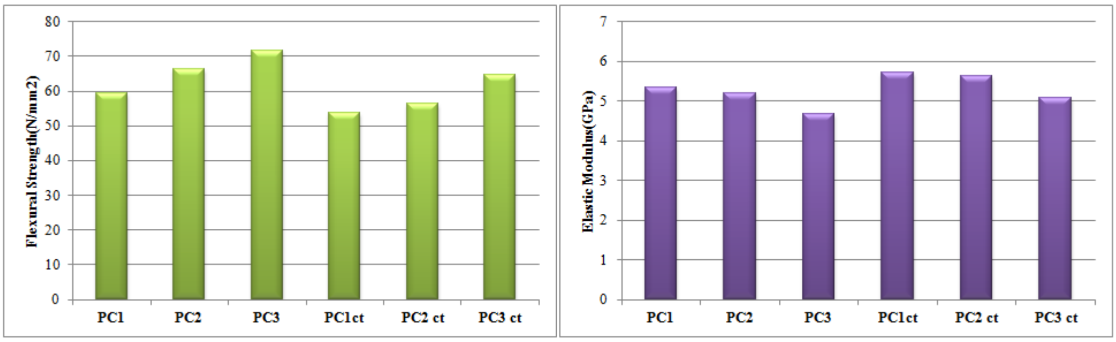

Figure 3. Bending properties of composite samples

In order to determine the properties of reinforcement-filling materials' and the polyester matrix interface in the manufactured composite samples a Scanning Electron Microscope (SEM., Zeiss Supra 40VP, Germany) was used to view the images. SEM images of untreated pine cone and chemically treated pine cone reinforced composites taken from a cracked surface are given in Figure 4.

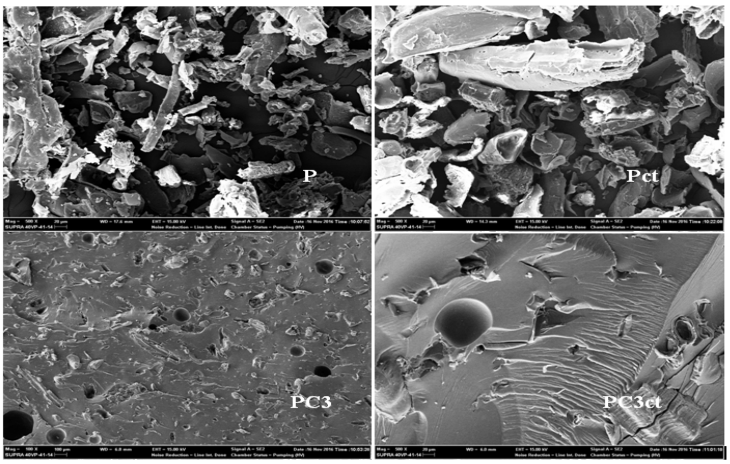

Figure 4. SEM images of raw material and composites

In Figure 4 abbreviations represent respectively P: untreated pine cone, PCt: chemically treated pine cone, PC3: untreated pine cone composite sample, PC3ct: chemically treated pine cone composite sample as indicated in Table 1. According to SEM images of both the chemically treated composite and the raw material it can clearly be said that treatment provided a good combination of matrix and fillers. This is because in the PC3ct image the pore size increased and stratification is more than the PC3 composite. It can also be seen that in PC3 the surface of the composite is covered with a layer of substances, which may contain some pectin, lignin and other impurities. The surface is not smooth, but covered with nodes and irregular stripes. After the chemical treatment of the PC3ct composite most of the lignin and pectin are removed causing a rougher surface.

Conclusion

Chemical treatment that was applied to increase the ratios of pine cones reduced the flexural strength but increased the elastic modulus. Increasing amounts of cones reduced the impact strength as supported by an increased amount of open porosity. It can be concluded that chemical treatment would increase the physical properties of composites while decreasing the mechanical properties.

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11

Management of Domestic Wastewater through Segregated Streams as an Aid towards Sustainability of Natural Resources and Sustainable Agriculture/Food Production

Bilsen Beler-Baykal

Abstract

Conventional domestic wastewater management is a linear open cycle process, where domestic wastewater generated from different household functions is mixed and collected in one single pipe, treated to remove constituents regularly regarded as "waste", and discharged into receiving media, "wasting" the valuable material and energy hidden in domestic wastewater. Segregation of domestic wastewater into various streams in the household lends a sustainable alternative for revaluating valuable components. Stream segregation starts with separate collection of streams which are different in terms of their character as well as their pollution potential at their point of generation, to be processed further for producing products to serve beneficial end-uses. Currently, segregation is practiced either as two-component separation as black (wastewater from toilet–bowls) and grey (all portions of domestic wastewater with the exclusion of toilet wastewater); or three-component/ECOSAN segregation as grey, yellow (separately collected urine) and brown (separately collected feces). Upon segregation and proper processing, nutrient-rich yellow water may be used as fertilizer, aiding sustainable agriculture, food production and landscape/green areas; brown/black water for energy and/or compost production; reclaimed grey water, corresponding to75% by volume, as an alternative source of water to be returned to almost any point in the water cycle, helping sustainability of natural resources. Stream segregation is an approach which promotes sustainability both through valorizing wastewater and through environmental protection.

Keywords: Stream segregation, Domestic wastewater, Sustainability through revaluating wastes, Water reclaimed from grey water, Fertilizers from human urine/yellow water

Introduction

Domestic wastewater management, in the form it is practiced at this time, is a linear open cycle process, where domestic wastewater generated as a result of different household functions is mixed and collected in one single pipe. The main idea is to treat wastewater following single line collection to free it from constituents which are regularly regarded as "waste", turn them into gas, liquid and solid end products, and discharge the treated effluent into a receiving medium. Under those circumstances, organic carbon is converted mainly into carbon dioxide, nitrogen into nitrogen gas, as gaseous products and released into the atmosphere, while the majority of phosphorus resides in the sludge which needs to be treated further. Although this approach has been used for decades as the main option to abate water pollution and safeguard the environment, it "wastes" the valuable material and energy hidden in domestic wastewater which could otherwise be valorized to help maintain environmental sustainability and upraise human welfare.

Alternative ways of wastewater management have been introduced in the recent years which make use of the conventionally "wasted" valuable components of domestic wastewater and use it as a source or a raw material to produce new products to benefit from. One of those alternatives, namely, stream segregation / ECOSAN (Ecological Sanitation), is based upon separation of domestic wastewater into various streams at their locations of origin to be processed further for producing valuable material (Otterpohl et. al.,2003, Beler Baykal, 2015), i.e. reclaimed water and fertilizers. Production of compost and energy are yet two other options when this practice is adopted (de Graaff, et. al, 2011, Tervahauta et. al, 2014).

This paper aims to highlight stream segregation and ECOSAN as a recent approach to revaluate a waste, namely, domestic wastewater, to create value out of it, while controlling water pollution at the same time, specifically focusing upon producing reclaimed water which can be utilized almost at any point in the water cycle and fertilizers which can serve various purposes like agriculture, landscape and urban greenery zones on one hand, while taking care of water pollution on the other. Such an approach will not only benefit sustainability of water resources but also will contribute to agricultural production, food security and promotion of greenery and landscape areas. A further aim is to open this option to the discussion of the multidisciplinary experts/community, to hear comments of experts representing interrelated disciplines upon the subject matter, and to search for collaboration around this perspective from a wide spectrum and diversified points of view.

Segregated Streams of Domestic Wastewater

Stream segregation/ECOSAN claims that domestic wastewater is not a waste to be discarded but a source to be revaluated, and is based upon separating various streams at their point of origin and avoiding mixing of those segregated streams throughout each step including storage and processing. In the process of segregation, streams which are different in terms of their character as well as their pollution potential are separated at the first point they are generated, stored separately without mixing, and processed to produce products for beneficial end-uses. As such, it is an option which starts the management process at the household level and is closely related to control at the source. Furthermore, it enables revaluation of valuable components in domestic wastewater, which is conventionally perceived as a waste.

Currently separation is practiced either as two component (black/grey) or three component/ECOSAN (yellow/brown/grey) segregation. In case of two component segregation, domestic wastewater is separated as black water and grey water, where grey water refers to all portions of domestic wastewater with the exclusion of toilet wastewater and black water to that portion coming from the toilet-bowl. With three component segregation, also and more commonly known as ECOSAN (ECOlogical SANitation) separation, the streams are yellow water which is separately collected human urine and brown water which is separately collected feces, in addition to grey water as described above.

Table 1 summarizes some characteristics and reuse of each stream. The greatest portion of domestic wastewater appears as grey water with 75% which contains organic matter and pathogens as significant pollutants. Yellow water is a nutrient rich stream containing majority of nitrogen (N), phosphorus (P) and potassium (K) in conventional wastewater, however it constitutes only 1% of the domestic wastewater volume. Brown water is just 0.1% by volume and is rich in organics and pathogens as well as containing appreciable amounts of phosphorus. Black water is that fraction of domestic wastewater which contains the entire toilet wastewater, that is urine, feces and flush water, making up 25% by volume, and is rich in organic matter, nitrogen, phosphorus, potassium and pathogens.

One very important issue to note about segregated streams is that all streams are renewable, and even if their quantities may change from one community to the other, they will be produced forever as long as mankind survives. This makes each segregated stream a dependable and consistent source of raw materials for their respective final products.

Table 1 - Characteristics and reuse of segregated streams of domestic wastewater (based on Beler-Baykal, 2015)

Stream	**Fraction**	**Volume%**	**Organic matter%**	**N %**	**P %**	**K %**	**Pathogens**	**Constituentsto be revaluated**	**Constituents to be removed**	**Valuable products**	**Final use**
Grey	Wash water (all except toilet bowl)	75	41	3	10	34	Low	Water	Organic matter Pathogens	Water	Flush water Irrigation Other water cycle uses
Yellow	Source separated urine	1	12	87	50	54	Very low	Nitrogen Phosphorus Potassium	Pharmaceutical?Hormones? Pathogens	Fertilizer	Agriculture Landscape Green areas
Brown	Source separated feces	0.1	47	10	40	12	High	Organics Phosphorus	Pathogens	Energy Compost	Energy Agriculture
Black	Urine Feces Flush water	25	59	97	90	66	High	Organics Nitrogen? Phosphorus? Potassium?	Pathogens?	Energy Compost?Fertilizer?	Energy Agriculture?

A Discussion of Stream Segregation in Households as a Sustainable Approach for Domestic Wastewater Management

Stream segregation is a recent domestic wastewater management concept and as it takes care of water pollution, it also enables the use of waste streams as raw material for useful products and aids sustainability of water resources and food production/agriculture through revaluation of "waste" material. One very important issue to realize is the fact that stream segregation is a concurrent route for valorizing wastewater and for safeguarding the environment through controlling water pollution, which actually constitutes the essential and ultimate aim of wastewater management. As such, stream segregation serves two main issues of sustainability. That is, both environment and natural resources are protected, and wastes are handled in such a way as to make them beneficial sources.

With stream segregation, the greatest portion of domestic wastewater ends up as grey water with 75%. Due to its low pollution potential, with only organic matter and pathogens to take care of and very low nutrient content, this is a much easier stream to reclaim as compared to conventional domestic wastewater which is expected to have much higher levels of organics and pathogens in addition to problematic nutrients, i.e. nitrogen and phosphorus. Reclaimed grey water may be returned to almost any part of the water cycle for reuse after proper treatment including uses like flush water, irrigation, car washes, firefighting, etc. Treatment options include extensive systems like constructed wetlands which may be preferred more in rural settings and compact treatment schemes like membrane bioreactors and rotating biological contactors which suit urban settings perfectly (Nolde, 1999 & 2005, Beler Baykal, 2015) One very useful practice is reuse of reclaimed grey water as flush water. Constituting about one fourth of the daily domestic water use, flush water is used for sweeping human excreta, a stream which carries the highly pathogenic agents, down the sewer systems, using water of potable quality. Obviously, this is a "waste" of high quality water which acts against sustainability of water resources, and replacement of potable water with reclaimed grey water for flushes will enable the use of three days' domestic water supply for four days. As an example, the quantity of water used for toilet flushing in the Turkish megacity Istanbul is estimated to be more or less equivalent to the water supply transferred from Buyuk Melen which is about 200 km away (Beler Baykal and Giresunlu, 2013). There are appreciable examples of reclaimed grey water use for toilet flushing like those described by Nolde (1999) and Giresunlu and Beler Baykal (2016). As exemplified here for flush water, the use of grey water as an alternative source of water will clearly help the sustainability of water resources to a considerable extent.

Yellow water constitutes only1% of the domestic wastewater volume but contains up to 87% of nitrogen and over 50% of phosphorus, which are two of the primary water pollutants which ironically make up two of the three major constituents of fertilizers. The entire potential of nutrients (nitrogen, phosphorus and potassium) in human excreta on a global scale is equivalent to 30-40% of the global fertilizer use. Moreover, nutrients from the excreta of one person on an annual basis are enough to produce about 200 kg of cereals per year, or roughly a large loaf of bread per day. The greatest portion of nutrients in domestic wastewater come from urine which can be used both via direct and indirect routes. While urine may be applied directly upon plants after storage for hygienic safety (Hoglund, 2001) and probably dilution, it has to be processed before application when indirect routes are selected. Ion exchange/adsorption, struvite precipitation and stripping/absorption are the most common methods employed for processing of urine for production of fertilizers. Different types of fertilizers may be produced through those indirect routes using source separated human urine as raw material including phosphorus rich struvite, nitrogen rich ammonium sulfate and nutrient enriched zeolites which is rich both in nitrogen and in phosphorus (Basakcilardan-Kabakci, et. al, 2007; Etter, et. al., 2011; Beler Baykal et. al., 2004, 2009, 2011; Beler-Baykal and Dogan, 2016, Kocaturk and Beler Baykal, 2012). Revaluation of this stream is clearly a very significant potential to combat hunger, and yellow water, only 1% of domestic wastewater, is a renewable source which will contribute to sustainable agricultural products as well as promotion of green areas.

Grey water is a renewable source of water as although its quantity varies from community to community, its production is inevitable as long as mankind survives on this globe. As a matter of fact, all other segregated streams, i.e yellow water & urine, brown water & feces, or black water & both urine and feces, are also renewable and will be generated obligately as a result of indispensible metabolic activities of mankind.

Stream segregation is actually a practice which demands a holistic approach and a thorough planning ahead of time, and necessitates collaboration of different disciplines including various branches of engineering like environmental, civil, mechanical, agricultural, chemical, in addition to planning, social sciences, management and economics among others. The first tier of sustainability is environmental. From the technical stand point, stream segregation necessitates a new type of infrastructure which should preferentially be planned a head of time. Depending upon the type of segregation adopted, toilets, flushes, piping, storage tanks, pumping and finally provisions for processing each stream for the production of the final end-product will have to be provided. This short list of tasks is to be undertaken by the engineering group. Planning of the path way of the "raw material", i.e. the "waste"water, is significant, additionally, planning regarding the final destination and final consumers of the end product ahead of time is also as crucial. Economic sustainability is the second tier of sustainability and economists and management experts will be the major actors here, not only for funds and marketing but also for financing the new approach through administrative incentives and economic instruments. Last but not the least, new alternatives to be employed by mankind would necessitate the acceptance by final consumers. Social sciences and education will play a major role within this context, taking care of social sustainability.

Concluding Remarks

Stream segregation is a plausible option for domestic wastewater management which aids sustainability of the world resources with additional benefits as compared to the conventional one. Upon segregation and proper processing, nutrient-rich yellow water may be used as fertilizer, aiding sustainable agriculture/food production; brown/black water for energy and/or compost production, constituting 75% by volume grey water may be reclaimed as an alternative source of water which may be returned to almost any point in the water cycle to help sustainability of natural resources. Stream segregation is an approach which promotes sustainability both through valorizing wastewater for various end-uses and through environmental protection.

Despite its value has been underestimated to date, the benefits it will provide in relation to environmental sustainability and its support for sustainability of natural resources is envisaged to make segregated streams/ECOSAN an acknowledged, and possibly a popular, route for domestic wastewater management in the future.

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12

Environmental and Economic Analysis of a Rainwater Harvesting System at Marmara University

Recep Önder Sürmeli

Abstract

Marmara University is located in Istanbul/Turkey; being part of the most urbanized city makes water consumption and management an important issue in the campus areas. The main campus of the Marmara University, Göztepe Campus, has 38 buildings that equal 20% (~28000 m^2) of the total university area (~140000 m^2), which give a chance to use rainwater harvesting (RWH) as an efficient and sustainable pathway for water management. According to the average precipitation of Istanbul (~813 mm/year); 85% collection and 70% storage efficiency will provide ~0.484 m^3/m^2 potential amount of RW that will be collected by the roofs during a year, which equals to the ~60% of the precipitation. The potential amount of harvestable RW will be 13610 m^3/year, which make RWH in the campus area an efficient and sustainable supplementary water source that give a chance for potable water saving and also economic and environmental benefits at the end.

Keywords: Rainwater harvesting, Water scarcity, Water footprint, Renewable water resources, Sustainable city

Introduction

Water is a scarce and valuable resource for most of the natural systems and human life. Conservation of it becomes very important due to the increasing demand with the population explosion, changing life standards, industrial activities, continuous economic growth and mostly because of the climate change (Rostad, Foti, & Montalto, 2016; Zhang et al., 2009). It directly affects the eligibility of life in many ways (Coombes et al., 2016). Therefore, protecting deficient and diminishing fresh water sources is significantly crucial under these stress-causing situations.

Rapid and unplanned urbanization causes problems due to high amount of water consumption; new treatment facilities and infrastructures have to be constructed for water supply, wastewater collection, stormwater drainage, and maintenance of them has to be done more than before because of overuse (Steffen et al., 2013). Consequently, in cities, as a natural resource water must be used rationally and reuse of it has to be mandatory now and for future generations. Rainwater harvesting (RWH) is a decentralized water management process (Zhang et al., 2009) that gives opportunity to solve one part of this huge problem and offers many advantages than the municipal water distribution system (Pacheco et al., 2017).

RWH is a sustainable, effective, economic, secure and environmental friendly method, which becomes widespread in rural and mostly in urban areas. Harvested water can be used for toilet flushing, air conditioning, landscape and crop irrigation, cleaning purposes and can be used as a drinking water supply after acceptable treatment (Domènech & Saurí, 2011; Harb, 2015; Reckinger et al., 2015; Rostad, Foti, & Montalto, 2016 ; Zavala, Vega & Miranda, 2016). RW can be collected from roofs of all kind of structure, land surfaces directly and rock catchments, and stored with natural and/or artificial puddles, constructed reservoirs and commercial storage tanks (Fletcher et al., 2008; Helmreich & Horn, 2009). There are three models for RWH: in situ RWH, external RWH and domestic RWH (Helmreich & Horn, 2009).

The roofs of the buildings can be used like a drainage basin to collect rainwater (RW). This approach is an essential part of the domestic RWH model. The key point on that remedy is to store and conserve the precious and expensive fresh water in a sustainable way. RWH also gives a chance to decrease water and carbon footprint for the urbanized areas (Zuberi et al., 2013). In addition, every cubic meter of water gained by this method decreases the discharged water to the sewage system with eliminating the stormwater entrance and reduces the pumping expenses for the water supply.

For efficient RWH, annual rainfall is the most important figure; magnitude and intensity of the precipitation are also key points to set-up a convenient RWH system. Those systems need a suitable roof or roof clusters for catchment, tank systems for storage, an effective distribution structure, enough annual precipitation for economic compensations and may include a treatment unit for the purpose of usage (Özölçer, 2016; Vieira et al., 2013; Zavala et al., 2016). The treatment process changes due to the aim of the RW usage and may include sedimentation, filtration, membrane modules, biological processes, infiltration and disinfection units (Fletcher et al., 2008).

In addition, RWH systems have many advantages: controlling of urban flooding, erosion and pollution problems, create a better microclimate, decrease the load on the water collection and the distribution cycle, renewing the groundwater sources and reduce the cost of water treatment and pumping (Harb, 2015; Vialle et al., 2015; Zavala, Vega & Miranda, 2016; Zhang et al., 2009).

The primary objective of this study is to evaluate the potential of the RWH system at the Göztepe campus of the Marmara University. This is the preliminary step to investigate, essentially the environmental gains and probable future economical profits of the RWH system. Thus, RWH reduces the water consumption, decreases energy demand and reduces the wastewater production. Göztepe Campus was chosen for this study because of being in the middle of a densely populated area and the campus is consuming significant amount of water. The esults obtained will turn on a pathway for to make a decision on RWH in the campus area and it will open a window for the other campuses of the Marmara University.

Methodology

The world population has an increasing trend, and it already passed 7 billion habitants. In parallel with that, Turkey and its most crowded city, Istanbul, has a continuous growth rate on the population (Figure 1). From 2007 to 2015, percentage of the population growth was 16.57% and 11.55% for Istanbul and Turkey, respectively. Göztepe Campus area (40°59'16.0"N - 29°03'10.0"E) is located in Kadıköy (Figure 2), which is one of the highly populated district of Istanbul, and has a similar trend on increasing population rates.

Istanbul has many different raw water resources including lakes, dams, and rivers in its borders and from other cities to get enough water for the megapol. Nowadays, potable water supplied to the city is changing 2400000-3000000 m^3/day. That huge amount of water is the main challenge of that fresh water problem. Collecting, storing, treating and distribution of the treated water to the city is a very costly, tough and long process to manage in a highly urbanized enormous territory.

In Istanbul, the potable water produced and distributed to the city by Istanbul Water and Sewage Administration (ISKI). ISKI has many different levels of water prices for a various kinds of consumers; for universities the price of one cubic meter potable water is 7.19 TL (2.23$ or 1.97€); that makes sense about the importance of RWH.

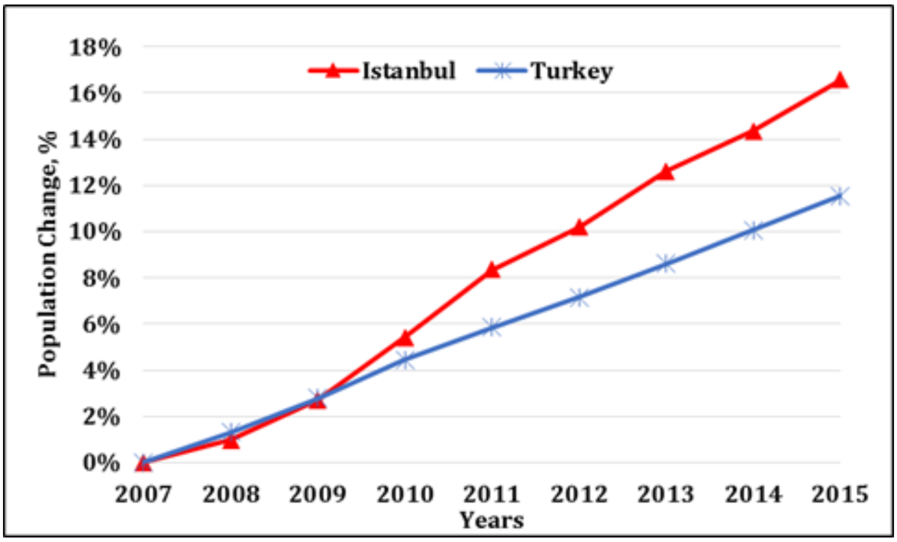

Figure 1. Population change of Turkey and Istanbul (2007-2015)

Total harvested RW was calculated according to the equation shown below.

$$V = P * A * C \quad (1)$$

where V is the harvested volume of the RW from the roofs; P is the annual precipitation amount; A is the surface area of the roof; and C is the runoff coefficient. C is dependent on the collection and the storage efficiency of the RW, which were assumed as 0.85 and 0.70 (Thomas & Martinson, 2007), respectively.

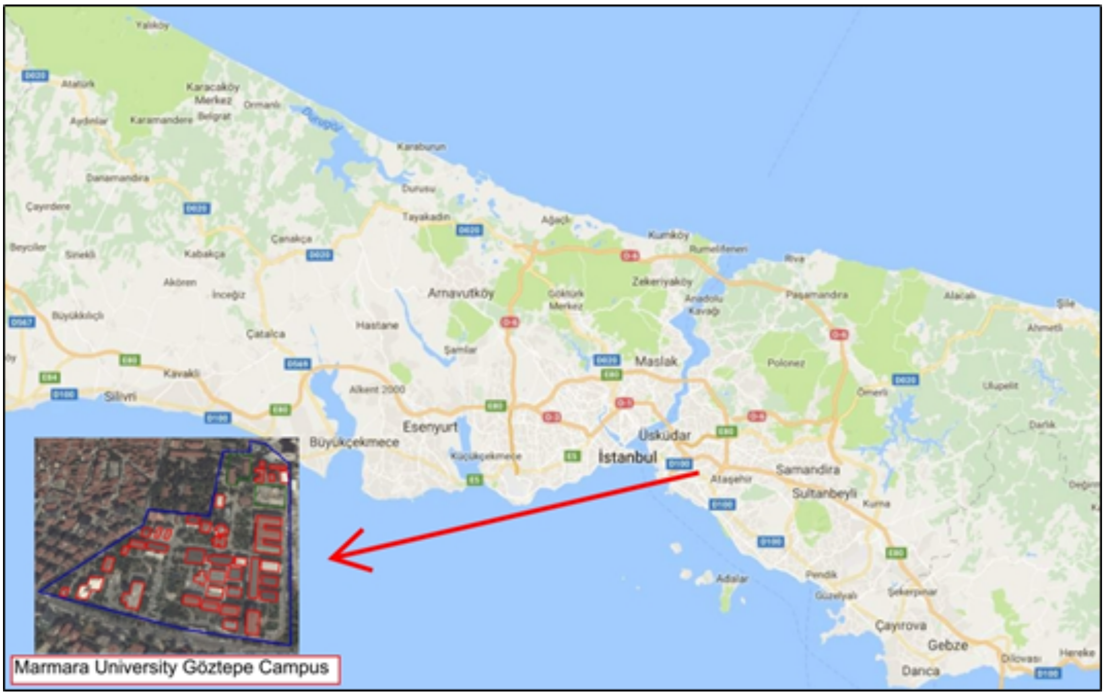

Figure 2. Map of Istanbul and the location of Göztepe Campus area

Findings and Evaluations

Overview of the Göztepe Campus was taken and created with the Google Earth Pro program. Figure 3 shows Göztepe Campus and roofs of buildings considered in this study. Total area of the Göztepe Campus is ~140000 m^2. In the campus, 38 buildings are suitable for RWH with the catchment area of their roofs. Those buildings cover 20% (~28000 m^2) of the total campus area. In that buildings, the pipes coming from the troughs of the roofs are located randomly (Figure 4). Some of them are connected to the rain collectors; others are directly open to the ground. All this pipes have to be connected to the RWH system systematically; the only way for an efficient management is a fully integrated system.

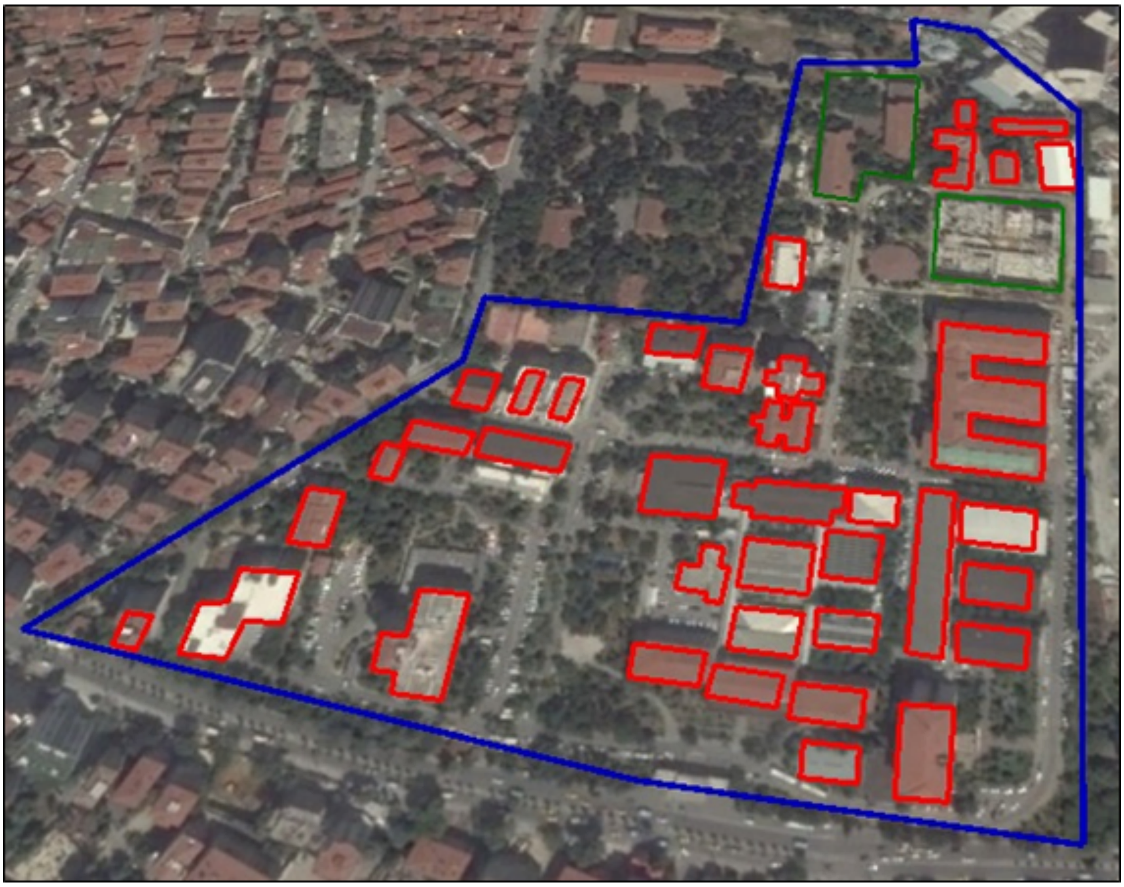

Figure 3. Marmara University Göztepe Campus overview (blue line is the border of the campus, red lines are the border of the roofs and green ones are the new buildings areas)

According to annual precipitation data taken from Turkish State Meteorological Service, Istanbul has ~813 kg/m^2/year precipitation (1950-2015) and Figure 5 presents monthly distribution of this amount. It is more than the Turkey's average (574 kg/m^2/year), which makes RWH more feasible for Istanbul than many other cities of Turkey. Besides that, Zavala et al (2016) studied RWH at a university campus in Mexico and found that, RWH is sustainable and efficient supplementary process for producing water. In that study, annual precipitation was 580 kg/m^2/year; that is 28% lower than Istanbul, that makes Istanbul has a better potential. In addition, according to Zuberi et al. (2013) and Özölçer (2016), RWH in the university campuses is an effective method should be supported.

Figure 4. Pipes connected to the roofs catchments (on the left: connected to the discharge system and on the right: directly open to the ground)

In accordance with the assumptions and the Equation (1), the roofs will collect ~0.484 m^3/m^2 potential amount of RW during a year. That is ~60% of the precipitation, which is equal 13610 m^3/year.

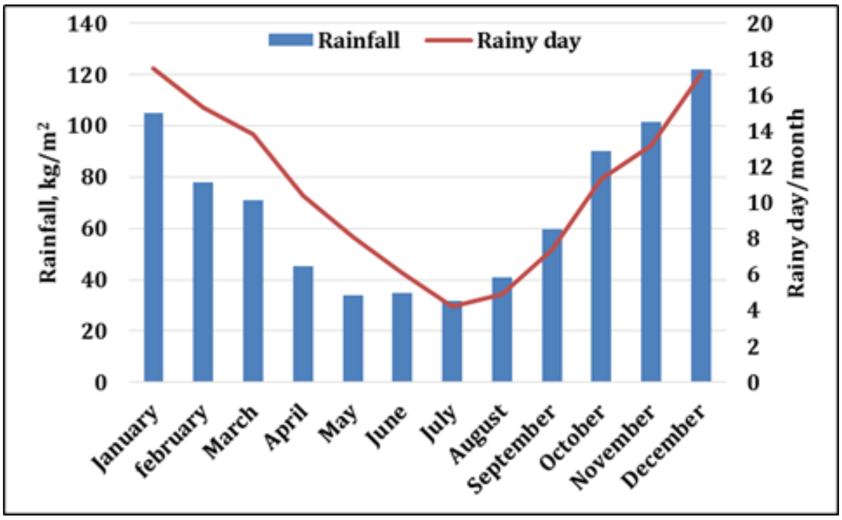

Figure 5. Monthly precipitation and number of rainy days of Istanbul

Conclusion

The preliminary results show that rainwater harvesting is an effective and sustainable system to provide a supplementary water resource for the Göztepe Campus of Marmara University. There will be many environmental and economical gains. Possible harvestable rainwater will be ~0.484 m^3/m^2, which makes up totally 13610 m^3/year, and this will decrease the water consumption cost of the university 97855 TL annually. This huge amount of water will be used after installing storage and distribution parts for irrigation and toilet flushing without any treatment. For other consumption options, a treatment module has to be applied to get an appropriate water quality. To establish how feasible is that system and to eliminate future bugs a pilot study should be started. A bunch of building will be chosen and a yearlong data collection period will give the best opinion for whole grid. Even if no action is taken after harvesting, all collected water from the roofs might be given to the soil for the aim of groundwater recharging.

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13

Environmentally Sustainable De-icer Management for an Airport

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Fatos Germirli Babuna

Abstract

The objective of this study is to evaluate the environmentally sustainable aircraft de-icer management strategies in an airport to lower greenhouse gas emissions by adopting life cycle assessment methodology. Sabiha Gokcen International Airport where, a formulation containing mainly propylene glycol is used as aircraft de-icer, is investigated. The effect of on-site and off-site de-icer recycling, application of various recycling rates and types of glycol on emissions are presented via "cradle-to-grave" perspective. When propylene glycol is used, annually 35892ton CO_2e is found to be generated. On the other hand, 60% on-site recycling of spent propylene glycol yields on average 17016ton CO_2e/year. Off-site recycling with 60% recycling rate reduces the original amount to 20965 ton CO_2e/year. The usage of bio-propylene glycol instead of conventional one is investigated generate 24776ton CO_2e/year. Finally 30, 20 and 10% off-site recycling of spent conventional propylene glycol yield 28433, 30916 and 33408ton CO_2e/year respectively.

Keywords: Airport, Carbon Footprint, Sustainability, De-icer, Life Cycle Assessment

Introduction

Developing strategies to achieve an environmentally sustainable aviation sector must cover not only the issues related to the flights, but also the management of airports and their supporting infrastructure must be considered. Only by doing so sound roadmaps towards environmental sustainability can be obtained. Some chemicals used in airports can cause long term negative impacts on environment (Ahrens, Norstrom, Victor, Cousins & Josefsson, 2015; Filipovic, Woldegiorgis, Norstrom, Bibi, Lindberg & Osteras, 2015). Chemicals applied for the removal of existing ice and/or protection against ice formation are called de-icers. De-icers are used on both runways and aircrafts. Commercial de-icing formulations contain either propylene glycol or ethylene glycol. Similar to European countries and United States (Gray, 2013), propylene glycol formulations are used as de-icers in Turkish airports. The glycol content of de-icers varies between 50 to 88 % (Johnson, 2012). Glycols are not persistent or bio-accumulative (Murphy, Wallace, Knight, Cooper & Sellers, 2015). However, they are the major contributor to organic pollutant content of wastewaters generated from the airports (Freeman, Surridge, Matthews, Stewart &

Haygarth, 2015; Switzenbaum, Veltman, Mericas, Wagoner & Schoenberg, 2001). Due to this fact surface waters near airports are adversely affected from the usage of de-icers (Turnball & Bevan, 1995).

Apart from glycol, additives such as corrosion inhibitors, wetting agents, thickening agents, surfactants, anti-foaming agents are also used in de-icer formulations for various purposes i.e. keeping the de-icing solution on the aircraft, preventing corrosion etc (Mohiley, Franzaring, Calvo & Fangmeier, 2015; Johnson, 2012; Murphy, Wallace, Knight, Cooper & Sellers, 2015). Although these additives has a contribution less than 1 % by weight (Johnson, 2012), due to their existence glycol based de-icer formulations have higher toxicities than the toxicity of glycol solutions alone (Hartwell, Jordahl, Evans & May, 1995; Cancilla, Baird, Geis & Corsi, 2003; Mohiley, Franzaring, Calvo & Fangmeier, 2015; Murphy, Wallace, Knight, Cooper & Sellers, 2015).

Sustainable management of de-icers in airports is of importance as various alternatives can be considered when dealing with this issue. Some measures can be taken to lower the amount of de-icer applications on aircrafts such as mechanical de-icing (infra-red de-icing, hot air blast etc.) (US EPA, 2002; Gray, 2013). Besides the usage of computerized spraying systems is also stated to reduce the amount of de-icers (US EPA, 2002). Airport operators must choose not only the correct alternative among different chemicals used as de-icers, but also consider proper disposal or recycling methods. It is known that only de-icers applied on aircrafts can be recycled. The current technology is not allowing the recycling of de-icers used in runways. If recycling of used aircraft de-icers is preferred, the airport operators must decide on the type of recycling (on-site or off-site) and the percentage of recycling. Since many parameters are involved, a holistic approach is required while making a correct decision. On the other hand, environmental impacts of a service, an activity or a product can be evaluated on a holistic perspective with the aid of life cycle assessment (LCA). Such an approach eases decision making process for operators, manufacturers etc by presenting qualitative outcomes.

On a global basis the aviation industry is responsible for 2 % of all the anthropogenic carbon dioxide emissions (Monsalud, Ho & Rakas, 2014). Unless necessary measures are taken, an elevation of up to 15 % in this percentage is expected by the year 2050 (Baxter, Wild & Sabatini, 2014; Whitelegg & Cambridge, 2004).

In this context the objective of this study is to evaluate the environmentally sustainable aircraft de-icer management strategies to the reduce greenhouse gas emissions of an international airport by adopting life cycle assessment methodology. For this purpose Sabiha Gokcen International Airport where, a formulation containing mainly propylene glycol is used as aircraft de-icer, is investigated. The effect of on-site and off-site de-icer recycling together with the application of various recycling rates and various types of glycol are evaluated by using life cycle assessment in a "cradle-to-grave" perspective.

Materials and Methods

Sabiha Gokcen International Airport is located on the Asian side of Istanbul. The airport currently provides service to approximately 30 million passengers annually.

Data gathered from the airport are fed to Airport Carbon and Emissions Reporting Tool (ACERT v3.1 calculation tool) (ACERT, 2016) developed by Airports Council International (ACI) to get the current greenhouse gas emissions (ACI, 2009). The airport operator is responsible for the greenhouse gas emissions arising from the following activities: the fuel usage for air-side vehicles and employee shuttles, de-icer usage, waste/wastewater processing, electricity and natural gas inputs. The evaluation based on ACERT v3.1 calculation tool is used to find out the contribution of de-icer usage to whole greenhouse gas emissions generated by the activities of airport operator.

Similar to the other Turkish airports, a formulation containing mainly propylene glycol is used as aircraft de-icer in Sabiha Gokcen International Airport. Besides propylene glycol, the formulation contains water and other additives.

The effect of on-site and off-site de-icer recycling together with the application of various recycling rates and various types of glycol are evaluated by using life cycle assessment. The life cycle assessment analysis adopted in this study has a scope ranging from production of energy and raw materials to usage and final disposal of aircraft de-icer. Therefore the results of a "cradle-to-grave" analysis is used to find out the greenhouse gas emissions arising from the de-icer production, usage of it on aircrafts in the mentioned airport and final disposal.

The unit greenhouse emissions adopted in this study are obtained from a literature source performed on life cycle assessment of aircraft de-icers in Western Europe (Johnson, 2012). Due to differences in national electricity footprints it is expected to get slight variations in unit emissions for Turkey. However as Turkish power footprint is very close to that of Western Europe such an adoption will not cause significant discrepancies. Johnson, (2012) indicates a narrow gap between no recycling and recycling cases for countries with high power footprints and vice versa. Turkish electricity footprint is smaller (ACERT, 2016) than that of Western Europe, therefore the gap between no recycling and recycling alternatives is expected to widen. The mentioned literature considers 1 ton of de-icer with an average 65 % concentration of propylene glycol as functional unit. CO_2 e emissions arising from propylene glycol application as de-icer is compared with 60 % on-site recycling of used de-icer and 60, 30, 20 and 10 % off-site recycling of spent de-icer. Variations in the recycling rates are expected to yield different levels of CO_2 e emissions. The reasons lying behind such a variation can mainly be due to the following factors: i. Producing lower amounts of de-icers with increased recycling rates leading to generation of lower amounts of CO_2 e emissions; ii) As recycling rates are increased less spent de-icer will be introduced to wastewaters causing lower CO_2 e emissions. Besides transportation of de-icer or spent de-icer will affect the CO_2 e emissions.

The following sequence is used for the production of propylene glycol: Natural gas and crude petroleum is processed to obtain naphtha. Naphtha is converted to propylene by steam cracking. Then propylene is passed through chlorohydrin processing to generate propylene oxide. Finally, propylene oxide is subjected to hydration to produce propylene glycol. Carbon footprint of the additives and water are obtained from ecoinvent (2010) in Johnson, 2012. For on-site recycling, spent de-icer is subjected to ultrafiltration, ion exchange, pH adjustment and distillation. For off-site recycling, spent de-icer is evaporated, thereafter steam distillation and thin film evaporation is applied. For further details of the life cycle assessment application one must refer to Johnson, 2012.

Results and Discussion

Among all the activities performed under the responsibility of airport operators electricity usage, fuel consumption of air-side vehicles and de-icer usage both for aircrafts and runways, have highest contributions of 42 %, 19 % and 18 % to the greenhouse gas emissions, respectively, as given in Figure 1. It must be noted that these percentages are obtained on the basis of the operations take place in the airport under investigation without considering a life cycle assessment approach.

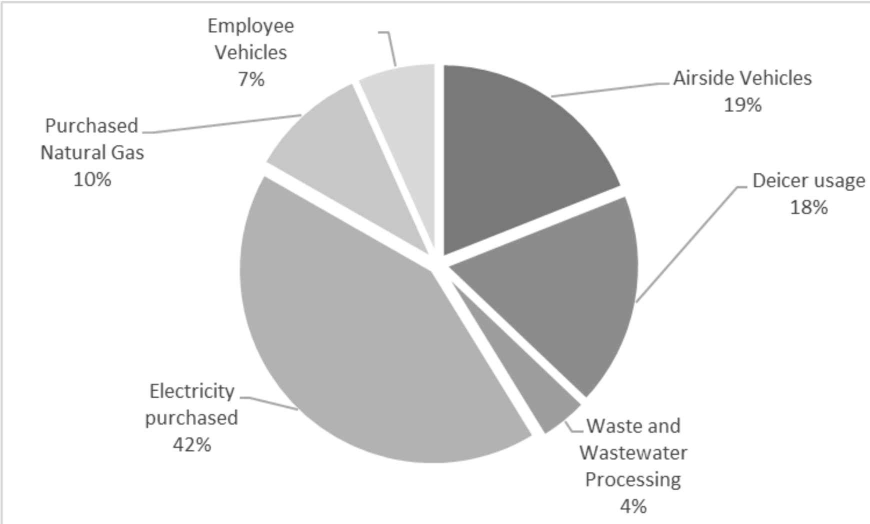

Figure 1. Percent distribution CO2 e emissions arising from activities performed by airport operators

All the greenhouse gas emission values presented in this study are based on carbon dioxide equivalent, in other words CO_2 e. "Carbon dioxide equivalent" or "CO_2e" is a term that describes various greenhouse gases, such as carbon dioxide itself, CO_2; methane, CH_4; nitrous oxide, N_2O; hydrofluorocarbons, HFCs; perfluorocarbons, PFCs; sulfur hexafluoride, SF_6; in a common unit.

The results obtained for greenhouse gas emissions by adopting the life cycle assessment to de-icer management is summarized in Table 1.

Table 1. Greenhouse gas emissions related to various de-icer management strategies via life cycle approach

Type of de-icer	Type of disposal	Recycling rate (%)	Unit greenhouse gas emissions (kg CO_2 e/ton de-icer)**	Minimum and Maximum greenhouse gas emissions (ton CO_2 e/year)	Reduction (%)**
propylene glycol	no recycle	-	3917	23930-47854	-
propylene glycol	on-site recycle	60	1857	11344-22687	53
propylene glycol	off-site recycle	60	2288	13976-27953	42
bio-propylene glycol*	no recycle	-	2704	16517-33035	31
propylene glycol	off-site recycle	30	3103	18955-37909	21
propylene glycol	off-site recycle	20	3374	20610-41220	14
propylene glycol	off-site recycle	10	3646	22272-44543	7

** propylene glycol made from plants **(Johnson, 2012)*

The usage of bio-propylene glycol (a type of glycol made from plant materials) instead of conventional propylene glycol (produced from petroleum) reduces greenhouse gas emissions by 31 %. Thus application of bio-propylene glycol results in average annual generation of 24776 ton CO_2 e. 30, 20 and 10 % off-site recycling of conventional propylene glycol yield 28433, 30916 and 33408 ton CO_2 e/year respectively.

Future Research Directions

As indicated earlier the unit greenhouse emissions adopted in this study are obtained from a literature source presenting the results of life cycle assessment of aircraft de-icers in Western Europe (Johnson, 2012). It is recommended to generate country specific data and perform a life cycle assessment by considering this data and local conditions (such as production flowchart of propylene glycol in Turkey, transportation issues etc.) to get more accurate outcomes.

Conclusion

The lowest carbon footprint is obtained when spent aircraft de-icer is recycled on-site by a rate of 60 %. This application lowers 35892 ton CO_2 e/year emissions to 1857 ton CO_2 e/year. After this comes 60 % off-site recycling that generates annually 2288 ton CO_2 e.

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14

Some Remarks on Sustainable Fisheries Management in Turkey

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Tomris Deniz
Nurdan Cömert

Abstract

Fisheries as an activity performed using natural resources are livelihood and strongly associated with the ecosystem. Hence it is a system which is characterized nesting complex relationship between society and the natural environment. Fisheries practices increased with the increase in the technological development and speed of globalization as well as environmental pollution. Therefore natural fish resources have been damaged for a long time. Most of fish stocks are fully fished and some are overfished. Focusing and monitoring on the sustainable use and conservation of renewable fish resources have a responsible manner for fisheries management. In simple terms, sustainable fisheries, known as harvested at a sustainable rate, means minimal ecosystem effects, healthy fish stocks and effective management. Turkey has an important spawning and fishing grounds for commercial fish species such as pelagic and demersal, so both large and small scale fishery are major economic activity. But yet it has been concerned that most of fish stocks are affected by overfishing and pollution in Turkey. For this purpose the aim of this study is to evaluate and improve the state of sustainable fisheries management in Turkey with the help of reported studies and official statistics regarding sustainable development for current and future practices.

Keywords: Turkey, fisheries management, sustainable fisheries.

Introduction

Fisheries, in simple terms, can be described as catching and evaluation of all kinds of living organisms by various methods in aquatic ecosystems. Since the Upper Palaeolithic (Childe, 1960), continued fishing activities with artisanal fisheries from that day to this, have reached the modern fishing environment using electronic equipment, equipment and information technology. During this long period, fishery, which has gained considerable economic value, naturally has significant effects on ecosystems and people. The life of all living organisms depends on natural resources and one of these natural sources is fishing which is not endless even though it is a renewable resource. At the point of ensuring the continuity of natural resources, the concept of sustainability became a current issue. The concept of sustainability in the global sense was first reported as "Our Common Future" by the World Commission on Environment and Development (WCED) in 1987. A general definition of sustainability is to supply daily needs by ensuring continuity of biological systems diversity and productivity without losing the ability of future generation's necessities. In the field of fisheries, sustainability means that fisheries can be made economically without harming the diversity and stocks of fish species. What is important here is that fishery can contribute to the global employment and animal protein supply without harming the ecosystem so that it can be maintained in an environmentally friendly manner.

Sustainable fisheries and the ecosystems in which they function provide significant benefits. These might be categorised as economic output, livelihoods, food security and ecosystem services. A transition to the sustainable management of fish stocks will ensure that these benefits are available to future generations (ISU, 2016). The past fifty years has seen a massive expansion in fishing capacity that has over-exploited many fisheries (Grafton, Kompas & Hilborn, 2007). Fisheries are an underperforming global asset. A recent study by the World Bank and Food and Agriculture Organization of the United Nations (World Bank & FAO, 2009) indicates that the difference between the potential and actual net economic benefits from marine fisheries is on the order of $50 billion ($10^9$) per year (Willmann & Kelleher, 2010). Global fishery production in marine waters was 82.6 million tonnes in 2011 and 79.7 million tonnes in 2012 (74.3 and 75.0 million tonnes excluding anchoveta). In these two years, 18 countries caught more than an average of one million tonnes per year, accounting for more than 76 percent of global marine catches (FAO, 2014). Today's fishing industry has the capacity to catch more fish than the amount of fish ecosystems can produce (Aksoy & Koç, 2012; Seçer *et al.*, 2010), and it was reported that 80% of them are collapsed, over-exploited, and are in the process of collapse as a result of work done by the Food and Agriculture Organization of the United Nations (FAO) today's fish stocks in 600 areas around the world (FAO, 2006).

Turkish coastline has four different characteristic seas with a rich marine biodiversity. From north to south: Black Sea, Sea of Marmara, Aegean Sea and Mediterranean Sea. In Turkish waters, the main fishery was targeted on small and medium pelagic fish for the Turkish coasts which are an important spawning ground for some migratory pelagic fish species such as Atlantic bonito, anchovy, bluefish and herring and also demersal fish (FAO, 2008; Gokturk, Deniz & Alıçlı, 2016). In marine capture fisheries the main stocks were anchovy, pilchard, horse mackerel, scad, whiting, grey mullet, blue fish, sprat, bogue, European hake, chup mackerel, red mullet, twaite shad, picarel, striped red, little tunny, frigate mackerel, striped bream, sand smelt, common sole, seabream, thornback ray, turbot, blue fin tuna, mackerel, tope shark, leer fish, saupe, red gurnard, annular bream, seabass, swordfish, white grouper, gar fish, saddled seabream, black scorpion fish, black seabream, saury, striped seabream, dentex, European barracuda, two banded bream, common seabream, gobies, dusky grouper, john dory, painted comber, blue spotted bream, albacore, brown meagre, greater amberjack, angel shark, corb, meagre, and shore rockling (FAO, 2008). However, the coastal and marine biodiversity also fish stocks of the Turkey was already under stress through a combination of heavy fishing, pollution, eutrophication, climatic fluctuations and the invasion of alien species due to the pressures exerted by mankind. Example of the Black Sea fish stock collapse is numerous and the unsustainable harvest of many fish species continuous today. Turkey is the most important country as to realize maximum fish production from the Black Sea. Pelagic fish species dominate marine landings in Turkey (Gokturk, Deniz & Oral, 2015).

Conservation and persistence of fish stocks are the basic principle of sustainable fisheries. However, many parameters are used in the calculation of sustainable fisheries. From this point of view, with using the data of marine fish landings, some remarks have been recommended to provide for sustainable fisheries in Turkey.

Data Collection

The data reported and evaluated in this study, especially, demersal and pelagic fish species which are commercially fished was obtained from Republic of Turkey Ministry of Food, Agriculture and Livestock, Turkish Statistical Institute and FAO (Food and Agriculture Organization of the United Nations) statistics as well as some reported studies about fisheries of Turkey.

Findings

General view of marine landings in Turkey

Turkish waters are important fishing grounds for both small and large scale fisheries regarding to abundance of commercial as well as migratory species. Variation of fish, invertebrates and total marine capture between 2000 and 2015 were illustrated in Figure 1. Approximately 200 fish species in the Black Sea, 260 fish species in the Marmara Sea, 417 species in Aegean Sea and 750 species in the Mediterranean Sea were reported (Froese & Pauly, 2016). However, approximately 66 fish species are commercially caught in Turkish waters and recorded their catch amount by Turkish Statistical Institute.

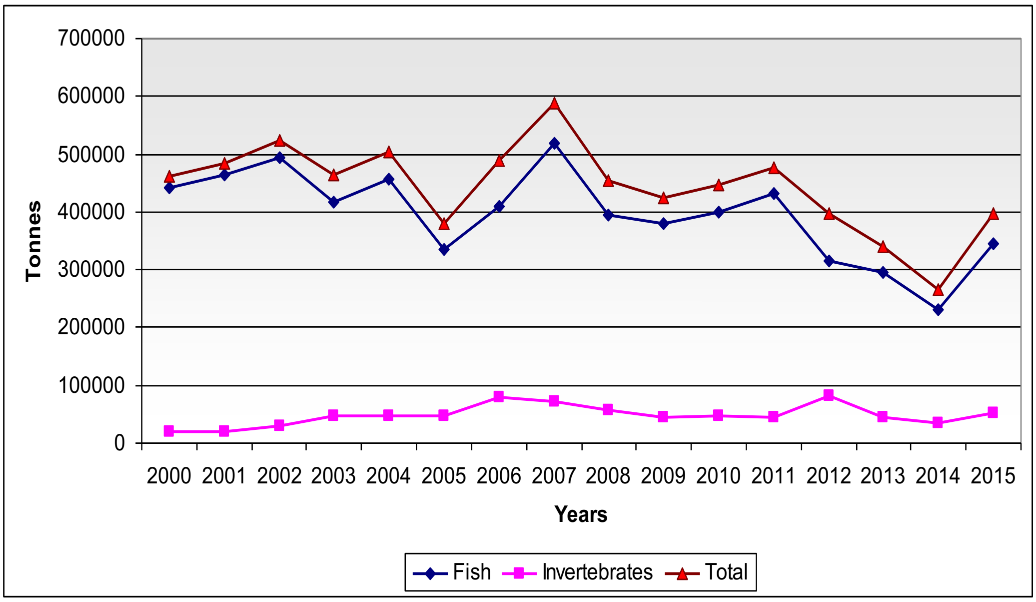

Figure 1. Fisheries landings of Turkey, 2000-2015 for amount of fish, invertebrates and total.

Anchovy (*Engraulis encrasicolus*, Linnaeus, 1758), pilchard (Clupeidae), horse mackerel (*Trachurus trachurus*, Linnaeus, 1758/*Trachurus mediterraneus*, Steindachner, 1868), Atlantic bonito (*Sarda sarda*, Bloch, 1793), blue fish (*Pomatomus saltatrix*, Linnaeus, 1766), sprat (*Sprattus sprattus*, Linnaeus, 1758) are the main commercial pelagic fish species (Figure 2), which have mostly caught by purse seine in Turkey. Anchovy takes the first place for pelagic fishery in Turkey, where especially caught from Black Sea coast, with the average of 246812 tonnes between 2000 and 2015 (TSI, 2015). Whiting (*Merlangius merlangus*, Linnaeus, 1758), European hake (*Merluccius merluccius*, Linnaeus, 1758), surmullet (*Mullus surmuletus*, Linnaeus, 1758), red mullet/goldon banded (*Mullus barbatus*, Linnaeus, 1758/*Upeneus sp.*) and turbot (*Scophthalmus maximus*, Linnaeus, 1758) are the main commercially important fish species for demersal fisheries in Turkey as a target or by-catch (Figure 3). There are some fishing methods for landing the demersal fish resources in Turkish coastlines, such as trawl, beam trawl, beach seine, gillnets, trammel nets and lines. The catch profile with respect to fishing methods, regions and species are summarized in Table 1. Especially, European hake, *Merluccius merluccius* is one of the most economically important exploited demersal fish species in both Europe and Turkey. In recent years, according to official data, it was clearly seen that the total of European hake landing of Turkey dramatically decreased day by day (20810 tons in 2001 and 706 tons in 2015).

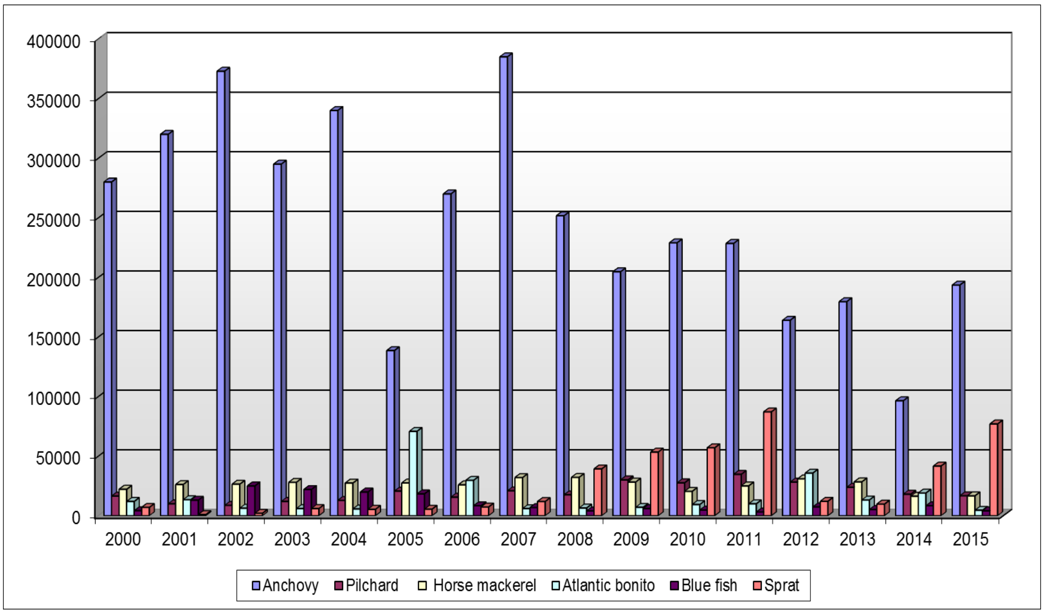

Figure 2. Main commercial pelagic fish species landings of Turkey between 2000 and 2015.

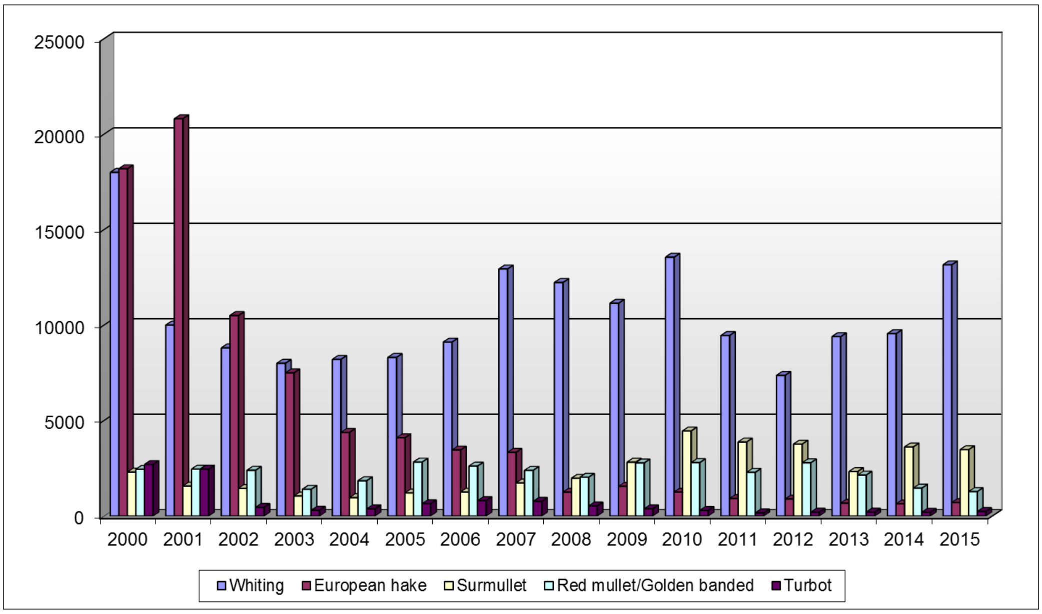

Figure 3. Main commercial demersal fish species landings of Turkey between 2000 and 2015.

Table 1. Marine catch profile with respect to fishing methods, regions and species.

Fishing method	**Region**	**Species**
Purse seine	Black Sea	Anchovy, horse mackerel, scad, Atlantic bonito, sprat, bluefish, chub mackerel, sardines.
	Sea of Marmara	Anchovy, Atlantic bonito, sprat, scad, bluefish, sardines
	Aegean and Mediterranean Sea	Sardines, chub mackerel, albacore, Atlantic bluefin tuna, little tunny, bullet tuna
Midwater trawl	Black Sea	Anchovy, horse mackerel, bluefish, sardines
Bottom trawl	Black Sea	Whiting, red mullet, turbot
	Aegean Sea	Mixed
	Mediterranean Sea	Mixed
Beam trawl	Sea of Marmara	European hake, whiting, red mullet (as a by-catch species)
Small-scale fisheries (gillnet, trammel net, longline, beach seine, traps)	Black Sea, Sea of Marmara, Aegean Sea and Mediterranean Sea	Mixed (i.e. Atlantic bonito, bluefish, whiting, turbot, red mullet, grey mullet, sparids, sole, swordfish and tuna-like)

There are 14340 fishing vessels licensed in Turkey according to statistics of the Turkish Statistical Institute such as trawler, purse seiner, carrier vessels, gillnetting, beam trawler, long liner and other vessels (TSI, 2015) (Figure 4).

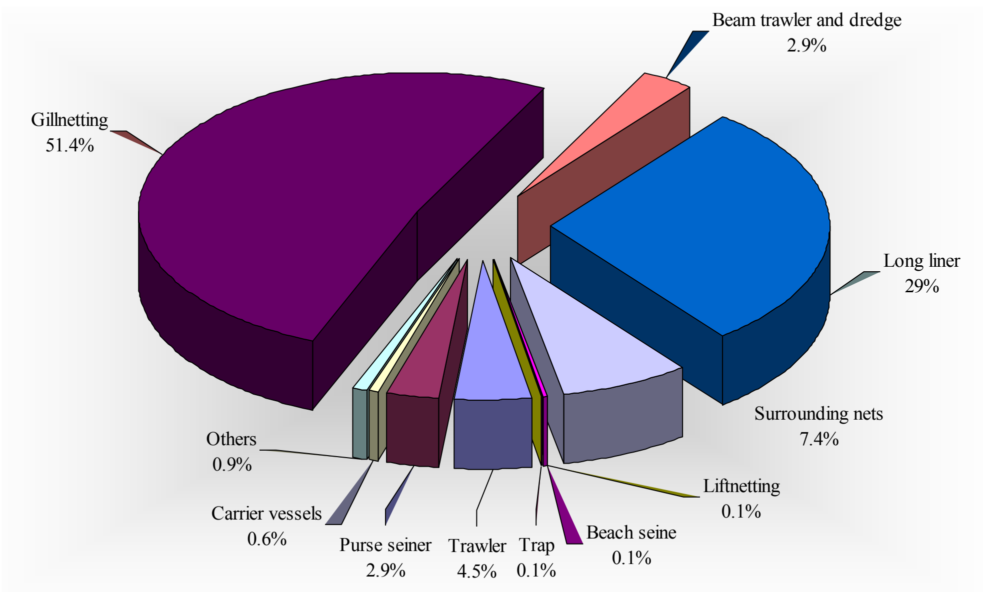

Figure 4. Distribution of licenced fishing vessels according to operating type.

Significant fluctuations were observed from 2000 to 2015 in total marine capture fisheries in Turkey (Figure 5). Pelagic species such as anchovy, bonito, horse mackerel, sardines and bluefish are dominated marine landings. Taking into consideration of total marine landings in Turkey it is observed that the dominant species is anchovy in biomass around 60–70 percent. As seen in Figure 5 the changes in catches of anchovy affected the total annual catch data in Turkey.

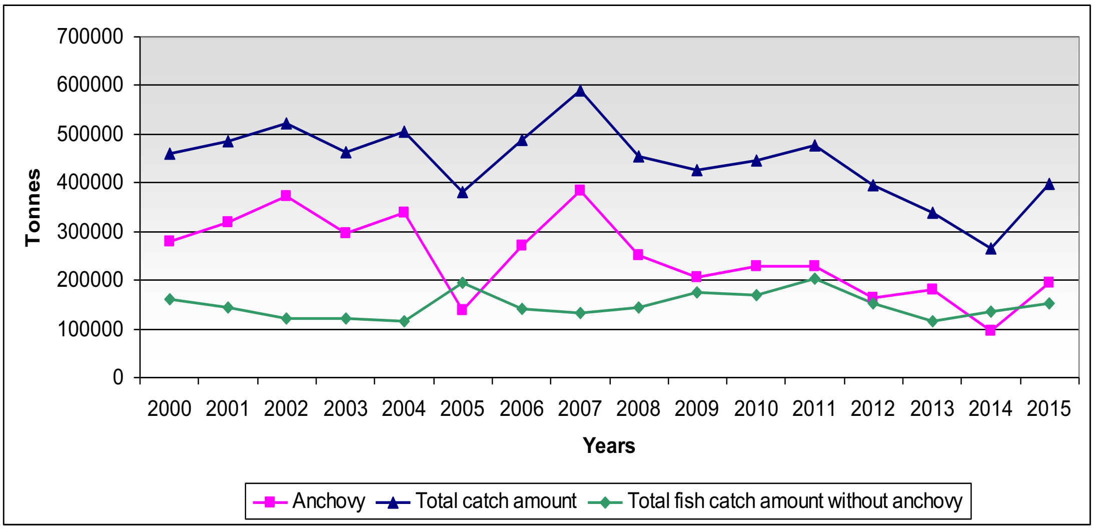

Figure 5. Fisheries landings of Turkey, 2000-2015 for amount of fish, invertebrates and total.

Remarks on sustainable fisheries management of Turkey

Republic of Turkey Ministry of Food, Agriculture and Livestock is the main state organisation responsible for fisheries administration, regulation, protection, promotion and technical assistance and all fisheries activities are based on the Fisheries Law No. 1380, enacted in 1971. Fishing regulations are based on minimum mesh size, minimum landing size or weight, closed area and terms for specified fishing gears and vessels, closed season, ban on catch to some species, gear restriction for identified species, gear or fishing method restrictions and some restrictions concerning pollutants. These management approaches have mainly focused on the control of fishing effort via restrictions on gear and equipment and the enforcement of fishing seasons.

Fisheries management can have many objectives, including conservation, political, social, and economic objectives. However, the most common advice is based on maximizing yield from a fishery (Maunder *et al.*, 2006). The size of the population, species growth rates and catch size in one region may be very different depending on the fishing area. Fished species are often regulated by prohibiting the landing of individuals below a minimum landing size. This size limit is typically set big enough that some individuals are allowed to reproduce before capture. According to Hilborn & Hilborn (2012), the growth rates can differ greatly from place to place, and the appropriate size limit in one part of the coast, or even one side of a rocky reef, may be different in another place. Regulations and management need to be very locally adapted (Göktürk, Deniz & Ateş, 2016). Minimum landing size should be controlled (Göktürk et al., 2017) and scientific studies should be carried out especially related to biological features of certain species to close the gap on this issue i.e. establishment of biological reference points to provide a basis for the conservation and sustainable use of catching species.

Enhancing information on ecosystems and the natural resource management are required. Accordingly, it can be promoted the use of equipment, fishing gears and methods to remove or reduce all unfavourable effects on populations, species, habitats and ecosystems, including capture of unmatured fish, accidental catches (by-catch or discard) and habitat destruction. It should be provided that catching data is regularly and easily accessible. Furthermore, the data should be included such as fishing times in day, hour etc., and structure of fishing gear in order to calculate detailed fishing effort. Additionally persistence of fish stocks by-catch and discard ratio should be provided and also be recorded statistically. In this context, the sanction power of existing regulations should be increased and international cooperation for the development of conservation/sustainable use policies achieved. Another important issue is to take precautions related to uncertainty and variability in natural resource and ecosystem dynamics. For instance, pelagic fish stocks, especially anchovy decreased due to comb jelly (*Mnemiopsis leidyi*, A. Agassiz, 1865) known as invasive species in Black Sea.

As an economic point of view another important contribution is highly migratory species (called as HMS) -not as catch amount- for the fisheries of pelagic species in Turkey since they have high commercial value. Highly migratory species is a term which has its origins in Article 64 of the United Nations Convention on the Law of the Sea (UNCLOS). These species, according to the 1982 convention, listed under Annex I (UNCLOS, 1982). Highly migratory species which are commercially caught in Turkey are albacore (*Thunnus alalunga*, Bonnaterre, 1788), Atlantic bluefin tuna (*Thunnus thynnus*, Linnaeus, 1758), little tunny (*Euthynnus alletteratus*, Rafinesque, 1810), Bullet tuna / Frigate tuna (*Auxis rochei*, Risso, 1810 / *Auxis thazard*, Lacepède, 1800), Swordfish (*Xiphias gladius*, Linnaeus, 1758) and Atlantic saury (*Scomberesox saurus*, Walbaum, 1792). These species are commercially fished by longline, purse seine, trammel net in Turkey. However the total catch amount of these species is recorded approximately 1% in the total fish landing of Turkey. Among them *T. thynnus* and *X. gladius* that are exported as fishery products have an importance economic contribution approximately with 39102935 $ (TSI, 2013). *T. alalunga*, *T. thynnus*, *E. alletteratus*, and *A. rochei*/*A. thazard* are commercially taken by purse-seine and they are also caught by longlines which are used for swordfish and leerfish fisheries as by catch. The swordfish fisheries are especially made by longline but the harpoon is still used in catching. *S. saurus* which is caught mostly by-catch as well as recreational fishing. Besides all these, driftnets have been extensively using for the fisheries of *X. gladius*, *T. alalunga* and *E. alletteratus* for a long time until it was banned totally in 2011. In addition, HMS are generally caught by mutually as by-catch and evaluated economically i.e. Atlantic bluefin tuna caught in swordfish longline (Deniz, Göktürk & Ateş, 2016). ICCAT (International Commission for the Conservation of the Atlantic Tunas) determines the country quotas of the member countries for Atlantic bluefin tuna fishery. Thus prohibitions such as minimum landing size, time and catch amount related to fisheries for this species in the Mediterranean basin are determined and implemented by ICCAT. Since Turkey is also member of ICCAT Atlantic bluefin tuna fishery is performed in Turkey based on ICCAT implementations. Swordfish fishery is also performed according to ICCAT regulations. However other implementations and prohibitions for tuna and tuna-like species are self-regulated based on ICCAT's recommendation by the member countries.

Another convention in which Turkey has been party to international agreements since 1954 is The General Fisheries Commission for the Mediterranean (GFCM). According to GFCM, Mediterranean and Black Sea fisheries are currently facing serious challenges, with roughly 90 percent of the scientifically assessed stocks considered to be fished outside safe biological limits, decreasing catches and shrinking fleets at the regional scale. In this context "Resolution GFCM/40/2016/2 for a mid-term strategy (2017–2020) towards the sustainability of Mediterranean and Black Sea fisheries" was prepared by GFCM (2016). The implementation of the proposed GFCM mid-term strategy towards the sustainability of Mediterranean and Black Sea fisheries will be guided by the following select principles which are in place at the FAO level:

- Best available knowledge: The provision of advice, including on the status and trends of stocks and fisheries, should be based on the best available knowledge, including scientific advice and relevant information emanating from a variety of sources and stakeholders. Efforts to collect all information available shall be ensured, and standards for assuring the quality of information should be applied wherever and whenever practicable and appropriate within Scientific Advisory Committee on Fisheries (SAC) and Working Group on the Black Sea (WGBS);
- Objectivity and transparency: The collection, analysis and dissemination of information on the status and trends of fisheries, ecosystems and marine environment should contribute to the transparent provision of the best scientific evidence available, while respecting any confidentiality requirements. Uncertainty associated with information on status and trends should be expressed, without detracting from the application of the precautionary approach, when data and information are incomplete. Information on activities towards the fight against illegal unreported and unregulated (IUU) fishing should be made available, respecting confidentiality requirements;
- Timeliness: The collection, analysis and dissemination of information on the status and trends of fisheries, ecosystems and marine environment, as well as information on IUU fishing, should be provided in as timely manner as possible;
- Participation and cooperation: The collection, analysis and dissemination of information on the status and trends of fisheries, ecosystems and marine environment, as well as information on IUU fishing, should account for all relevant participants in the preparation, analysis and presentation of scientific advice and conclusions. Relevant participants may include, inter alia, representatives of GFCM Contracting Parties and Cooperating non-Contracting Parties (CPCs), relevant international, non-governmental and civil society organizations. The cooperative network established by the GFCM through the adoption of various MoU would be relied upon, having regard to the cross-sectoral nature of the strategy;
- Adaptability: The collection, analysis and dissemination of information on the status and trends of fisheries, ecosystems and marine environment, as well as information on IUU fishing, should be adaptive enough to permit adjustments, as necessary, to ensure their effective support of fisheries management based on the most recent scientific advice available.

Conclusions

Sustainability that involves the environmental, social and economic conservation issues of ecosystems and human activities, and fisheries management that focuses on harvested species, are at an admitted crossroad. Fishery products are one of the most-traded food resources worldwide. In order to protect the stocks of commercial importance species and to ensure their sustainability, it is necessary to obey the regulations because, effective control of these prohibitions have a great importance for conservation of stocks in terms of sustainable fisheries. For this reason, it is beneficial to carry out continuous monitoring studies within the fishing periods in order to protect the stocks by regulating the fisheries strategies of the species having commercial importance in the fisheries sector. Therefore, these monitoring activities will also play a positive role in maintaining and sustainability of the precise ecological balance, which is linked each other. In a social point of view, effective efforts should be made for conserving marine biodiversity and sustainable use of resources as well as preventing overfishing.

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Engineering Approaches on Sustainability

In general terms, sustainability is the act of meeting our own needs today without compromising the ability of future generations to meet their own needs (World Commission on Environment and Development, 1987). Obviously, the ability of natural resources and environmental systems to support our needs is limited. Therefore, the major challenge for engineers today is to design and/or operate systems that use energy and natural resources sustainably. Designing for the environment is crucial. This book presents the recent engineering approaches to sustainability from research and practice.

The chapters included in this volume are from the first International Sustainability Congress organized by International Center of Sustainability (ICS) between 1-3 December 2016 in Istanbul, Turkey. All chapters are peer-reviewed by both the editors and at least two independent scholars from fields relevant to the manuscript's subject area. ICS is a research and academic center for sustainability founded in 2015 and dedicated to build resilience of communities and ecosystems to environmental and socio-economic risks. ICS has an integrated approach and defines sustainability not only in terms of environment but also in terms of socio-economic process. Its mission is to produce information, to research and to practice at Micro and Macro levels in Sustainable Development with a holistic and cross-disciplinary approach.

ISBN 978-0-9932118-2-9

IJOPEC PUBLICATION
London Istanbul

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