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DOÇ. DR. MİHRİBAN KALKANCI

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FUZZY L TYPE ENVIRONMENTAL RISK ASSESSMENT METHOD WITH MULTI-CRITERIA DECISION MAKING APPROACH

***Murat OTURAKÇI*[1]**

1 Dr. Öğr. Üyesi, Adana Alparslan Türkeş Bilim ve Teknoloji Üniversitesi, Endüstri Mühendisliği Bölümü

1. INTRODUCTION

Environmental risk assessments have become significantly important due to the increased level of global warming, industrialization, and legal requirements for the companies. Especially mandatory regulations about the environment lead companies to take immediate precautions according to their risk assessment methods. Assessing environmental risks is vitally important since certain chemicals may have a disastrous effect when it has released in nature. Certain hazards can affect the environment and human health and exposure to certain chemicals may change the landscape forever. Thus, environmental risk assessments are needed to perform to annihilate the potential hazards.

There are many qualitative or quantitative risk assessment methods in literature such as Failure Mode and Effect Analysis (FMEA), Hazard and Operability Methodology (HAZOP), Fault Tree Analysis (FTA), Event Tree Analysis (ETA), X Type Matrix, L Type Matrix, etc. All of those methods have a common objective as prioritizing the risks after the identification steps. Since the introduction of risk assessment methods, new approaches were attempted to develop to obtain minimum subjective results. In risk assessment literature, many studies take advantage of Multi-criteria Decision Making (MCDM) methods, fuzzy logic, or both. Cho et al. (2002) developed a new approach by using fuzzy concepts into classic risk assessment frameworks. The authors introduced new forms of fuzzy membership curves to minimize the subjective judgments of risk parameters. Xu et al. (2002) proposed a fuzzy logic-based FMEA with a prototype assessment expert system to overcome the limitations of the classic method. Authors stated that the new approach provided a more realistic and flexible reaction of the real situation and interdependencies among various failure modes and effects can be explored. Sadiq and Husain (2005) developed and assessed a hierarchical model of aggregative environmental risk for drilling waste discharge scenarios for disposal into the marine environment. In the study, parameter scales are defined as triangular fuzzy numbers to minimize the subjectivity of definitions and Analytical Hierarchy Process (AHP) is used for prioritizing the risks. Sharma et al. (2005) proposed a systematic FMEA by using fuzzy linguistic modeling. To prove the applicability of the study, the developed approach is implemented in the paper industry. Tesfamariam and Sadiq (2006) presented a new risk assessment method by using a risk-based fuzzy analytic hierarchy process (F-AHP) to guide decision-making under vagueness type uncertainty. The proposed method is applied to risks that occur from three generic types of drilling fluids for offshore oil operations.

Kaya and Kahraman (2011) proposed an integrated AHP–ELECTRE method for environmental impact assessment. The authors determined the weights with fuzzy AHP; assessed the environmental impacts with fuzzy ELECTRE and ranked the alternatives by using fuzzy dominance relation (FDR) methodology. Jozi et al. (2012) developed a methodology for environmental risk assessment by using integrated Shannon's Entropy–TOPSIS in Iran. In the study, risks are determined under classifications such as natural events and environmental risks, and they were evaluated under three parameters such as severity, probability, and vulnerability. Liu et al. (2012) proposed a new risk assessment method by using FMEA and VIKOR under fuzzy environment. Parameters of the risk factors are expressed as linguistic variables and extended VIKOR was used for prioritization. Guneri et al. (2015) provided fuzzy AHP for selecting the best risk assessment method in occupational health and safety operations for SMEs. Dağsuyu et al. (2016) developed fuzzy FMEA rules for the sterilization unit of a large hospital and new FMEA classes are proposed. Muhammet Gul et al. (2017) developed a new two-staged fuzzy multi-criteria risk assessment approach in a hospital. In the study fuzzy AHP was used for weighing risk parameters and the fuzzy VIKOR approach was applied for prioritization of hazards. M Gul et al. (2018) presented a risk assessment for the construction and operation period of wind tribunes. In the study, fuzzy AHP was applied to determine the weights of the Fine-Kinney parameters, and fuzzy VIKOR was used to prioritize the hazards. Hu et al. (2018) established a fuzzy comprehensive evaluation (FCE) based on the analytic hierarchy process (AHP) model. Karasan et al. (2018) introduced a safety and critical effect analysis method by integrating Pythagorean fuzzy sets. FMEA and Fine-Kinney methods' parameters were used in the study. Kokangül et al. (2018), developed an environmental impact assessment for a general use evaluating environmental aspects by impact category.

Regular risk assessment methods are used to assess the environmental risks of the companies. In addition to those, developing new assessment methods become a necessity for environmental issues since prioritization and evaluation of those methods become inadequate due to subjective evaluations. To understand the potential hazards of the risks, environmental risks have to be evaluated under certain impacts. Existing environmental risk assessment methods consider environmental risks thoroughly but an environmental risk could be harmful under many aspects such as air, soil, water, flora, or fauna. To fill this gap, the main aim of this study is to develop and implement a new approach for an environmental risk assessment by integrating the Multi-criteria Decision Making (MCDM) Approach with the conventional L-Type Risk Assessment Method. This study presents an original approach by assessing risks with the fuzzy L-Type approach to the categories of environmental impact categories of Air, Soil, Water, Flora, and Fauna. AHP method is used for weighing the importance of environmental impacts as an MCDM method and the Fuzzy L-Type method is developed to assess the risks. The developed approach is applied to environmental risks of construction activities of a medium-sized steel company to present the applicability of the method. Assessing risks under different environmental impacts with the fuzzy logic approach is the main contribution to the literature and implementation of the new approach shows the usability for practitioners as well as researchers.

2. MATERIAL AND METHODS

In this study, the environmental risks of construction activities of a steel plant company are identified with the occupational health and safety specialist of the company. In table 1, environmental risks and their explanations are presented.

2.1. AHP Method

AHP method originally developed by Thomas Saaty as a multi-criteria decision-making method (MCDM) (Saaty, 1980). In the AHP, the first problem and aim are defined. Then the main and sub-criteria with alternatives are produced. In order to create interaction between criteria and alternatives, a hierarchical structure needs to be formed and binary comparisons are made according to a comparison table that is presented in Table 1. (Saaty, 1980)

Table 1. Pairwise Comparison Table (Saaty, 1980)

Rating	Description
1	Equal importance
3	Moderate importance of one over another
5	Strong importance of one over another
7	Very strong importance of one over another
9	Extreme importance of one over another
2, 4, 6, 8	Intermediate values
Reciprocals	Reciprocals for inverse comparison

After binary comparisons are performed by decision-makers, the consistency ratio for formed matrix needs to be calculated by dividing the consistency index to the random index (Saaty, 1980). Consistency ratio is calculated by dividing consistency index to random index while the random index is formulated based on the number of criteria (n) and consistency index (CI) is calculated by deducting the number of criteria (n) from the largest eigenvalue of the considered matrix (λ_{max}) and dividing it to n-1. Consistency ratio has to be less or equal to ten percent, if contrary, comparison matrix has to be reviewed (Saaty, 1980)

2.2. L Type Method

In the conventional L type (5x5) method, the probability of occurrence of the risk and its severity are evaluated together. Probability and Severity scale of L type matrix method are presented in Table 2. With the multiplication of probability and severity values of certain risks, Risk Priority Number (RPN) is calculated to evaluate the risks. In Table 3, the RPN classification and its description are presented.

Table 2. Probability and Scale of L Type Matrix (Ceylan and Başhelvacı, 2011)

Value	Probability Description	Severity Description
1	Almost never (once in a year) / Unexpected	No loss for work hour; Need first aid/ No financial damage
2	Very Rare (couple times in a year), only in abnormal situations / Lowly possible	No loss for work day; needs an outpatient treatment / Financial damage ≤ 10.000 TL
3	Rare (once in a month) / Possible	Lightly injured, needs an inpatient treatment/ 10.001 TL ≤ Financial damage ≤ 50.000 TL
4	Frequently (once in a week) / Highly possible	Seriously injured, long time treatment, occupational treatment/ 50001 TL ≤ Financial damage ≤ 100.000 TL
5	Most frequently(everyday)/ Almost certain	Death, permanent incapacity of work / Financial damage ≥ 100.001 TL

Table 3. RPN Classification of L Type Matrix
(Ceylan and Başhelvacı, 2011)

Class Description	Class Interval	Class
Negligible Risks	RPN=1	1
Acceptable Risks	2≤RPN≤6	2
Mid-Level Risks	8≤RPN≤12	3
Important Risks	15≤RPN≤20	4
Unacceptable Risks	RPN=25	5

2.3. Developed Approach

Steps of the new approach are illustrated in Figure 1.

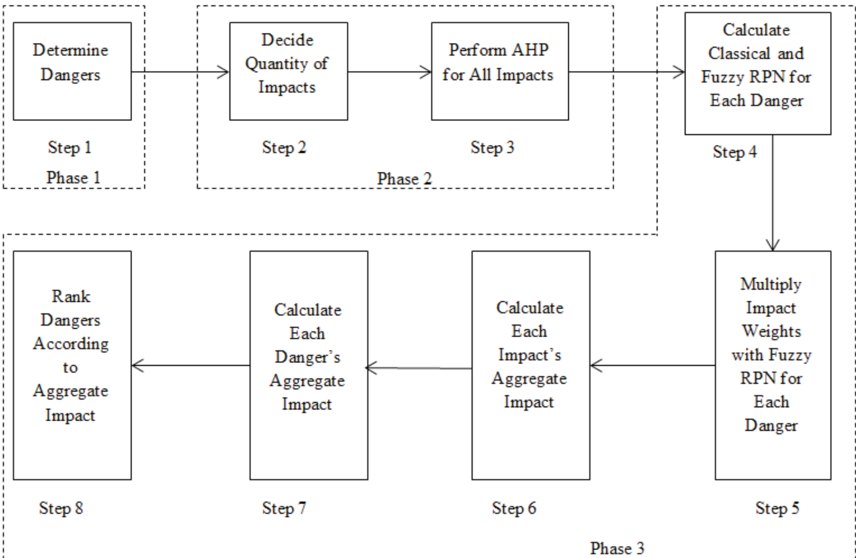

Figure 1. Steps of the New Approach

Step 1 is the determination of dangers which should be done with the occupational health and safety specialists. In Step 2, environmental impact categories should be determined. In this study, environmental impacts are decided as Air, Soil, Water, Flora, and Fauna. After determination of the impacts, In Step 3, according to the AHP steps that are given in section 2.1, are applied to determine weights of impact categories. In Step 4, to minimize the subjectivity of the evaluations in the classic method, fuzzy values of the L Type are obtained by using MATLAB, and fuzzy linguistic probability and severity values are presented in Table 4.

Table 4. Fuzzy Linguistic Probability and Severity Values of L Type Matrix

Probability		Severity	
Value	Fuzzy Linguistic Value		Fuzzy Linguistic Value
Very low	(1, 1, 2)	Very Slight	(1, 1, 2)
Low	(1, 2, 3)	Slight	(1, 2, 3)
Medium	(2, 3, 4)	Medium	(2, 3, 4)
High	(3, 4, 5)	Critical	(3, 4, 5)
Very High	(4, 5, 5)	Very Critical	(4, 5, 5)

By using fuzzy linguistic probability and severity values, fuzzy RPN classifications are obtained and presented in Table 5.

Table 5. Fuzzy RPN Classification of L Type Matrix

Class Description	Class Interval	Class
Negligible Risks	(1,1,2)	1
Acceptable Risks	(1,4,8)	2
Mid-Level Risks	(6,10,15)	3
Important Risks	(12,17,22)	4
Unacceptable Risks	(20,22,25)	5

After calculating fuzzy RPN values in step 4, the weights of each environmental impact category are multiplied with the fuzzy RPN value of related risk in step 5. Then, in steps 6 and 7, the sum of impacts and dangers are calculated to rank the risks in step 8.

3. CASE STUDY

Phase 1: Determine Dangers

In this study, the developed approach is applied to the environmental risks that occur in the construction sector. Hence, general risks such as scaffold collapse, falling off or occupational risks that occur from excavations were not taken into consideration. Environmental risks are determined with the occupational health and safety specialist team of a medium-sized construction company and risks are presented in Table 6.

Phase 2: Decide the Quantity of Impacts

Risks that are taken into account are analyzed with an environmental perspective in this study. Parameters in ISO14001 are taken into consideration in the determination of the quantity of impacts in this study since ISO 14001 is one of the most popular and reliable environmental standards in the world (McGuire, 2014). Parameters of air, soil, and water are taken from ISO 140001 while flora and fauna parameters are taken from literature since Kokangül et al. (2018) investigated environmental risk parameters in their study. Environmental risks are evaluated whether they affect parameters of air, soil, water, flora or fauna with the occupational health and safety specialists and presented in Table 6. In Table 6, "x" represents the effects of the risks.

Table 6. Risks and Quantity of Impacts

Risk No	Risk Explanation	Air*	Soil*	Water*	Flora#	Fauna#
R1	Mass Wasting		x	x	x	x
R2	Contamination of paint residues to soil	x	x	x	x	x
R3	Leaving construction and demolition waste to the agricultural fields	x	x	x	x	x
R4	Dissemination of harmful gases into the environment in the excavation process	x			x	x
R5	Dissemination of harmful gases into the environment of the excavation truck	x			x	x
R6	Wastewater in construction field		x	x	x	x
R7	Emission of particulate matter consisting of sand, cement, lime, etc.	x	x	x	x	x
R8	Dust formation during destruction of constructions	x	x		x	x
R9	Use of chemical components contained in building materials	x	x	x	x	x
R10	Fire due to flammable insulating materials	x	x	x	x	x
*ISO 14001 #Kokangül et al. (2018)						

Perform AHP for All Impacts

As can be seen in Table 6, environmental risks that occur from construction activities have different effects on the environment. In addition to that, each parameter has a different level of importance. Hence, the importance of risks is determined with the AHP method according to the binary comparisons of decision-makers. Results of AHP presents that importance weights of parameters are 0.2337; 0.4615; 0.0578; 0.1506 and 0.0964 for air, soil, water, flora, and fauna respectively. The consistency index is calculated as 0.06 and since it is less than 0.10, importance weights are used in this study.

Phase 3: Calculate Classical and Fuzzy RPN for Each Danger

Calculate Classical RPN for Each Danger

L Type risk assessment method is used in this study to evaluate risks. L Type Risk Assessment according to impacts is presented in Table 7. According to Table 7;

➢ "Dust formation during destruction of constructions" is the most important risk while "Leaving construction and demolition waste to the agricultural fields" is ranked last according to the "Air" impact.

➢ "Dust formation during destruction of constructions" is the least important risk while "Leaving construction and demolition waste to the agricultural fields" is ranked first according to the "Soil" impact.

➢ "Wastewater in construction field" is the most important risk while "Emission of particulate matter consisting of sand, cement, lime, etc." and "Fire due to flammable insulating materials" are ranked last according to "Water" impact.

➢ "Mass Wasting" is ranked first while "Dissemination of harmful gases into the environment of the excavation truck" and Emission of particulate matter consisting of sand, cement, lime, etc." are ranked last according to "Flora" impact.

➢ "Mass Wasting" is ranked first while risks that have an RPN score of 2 are ranked last according to the "Fauna" impact.

After assessing all risks according to the impacts, total risk scores for each risk are calculating by adding each related RPN impact score and results are presented in Table 7. According to the total risk scores; "Mass Wasting", "Contamination of paint residues to soil" and "Leaving construction and demolition waste to the agricultural fields" are found the most important risks respectively and "Dissemination of harmful gases into the environment of the excavation truck" is ranked last with a total risk score of 12.

After assessing risks according to total risk scores, weighted total risk scores are calculated by using AHP weights of impacts that are given in Phase 2 (Step3). Each RPN score of each risk is multiplied with related AHP weight and a weighted total risk score is calculated. For instance, the weighted total risk score of "Mass wasting" is calculated as "15*0.46 15+6*0.0578+12*0.1506+4*0.0964 = 9.4619". Weighted total risk scores of risks are presented in Table 7. According to the results, rank orders of 4 out of 10 risks are changed with a weighted total risk score.

In Table 7, environmental impact scores are assessed as well. Total impact scores are calculated as 64; 66; 36; 52; 37 for air, soil, water, flora, and fauna respectively according to the sum of all defined risk scores. In addition to that, weighted total impact scores are calculated and scores of 14.96; 30.46; 2.08; 7.83 and 3.57 for air, soil, water, flora, and fauna are found respectively. These impact scores present that, soil and air are the most affected impact categories due to construction activities.

Table 7. Application of L Type Risk Assessment

Risk #	Environmental Risks	Air				Soil				Water				Flora				Fauna		Total Risk Score	Rank			Weighted Total Risk Score	Rank
		(0.2337)				(0.4615)				(0.0578)				(0.1506)				(0.0964)							
		O	S	RPN	**Rank**	O	S	RPN	**Rank**	O	S	RPN	**Rank**	O	S	RPN	**Rank**	O	S	RPN	**Rank**				
1	Mass Wasting					3	5	15	**2**	2	3	6	**2**	3	4	12	**1**	2	2	4	**1**	37	1	9,46	**1**
2	Contamination of paint residues to soil	1	3	3	**6**	3	4	12	**3**	2	3	6	**2**	3	3	9	**2**	1	2	2	**3**	32	2	8,13	**3**
3	Leaving construction and demolition waste to the agricultural fields	1	2	2	**7**	4	4	16	**1**	2	2	4	**3**	2	3	6	**3**	1	2	2	**3**	30	3	9,18	**2**
4	Dissemination of harmful gases into the environment in the excavation process	3	3	9	**3**									2	2	4	**4**	2	2	4	**1**	17	9	3,09	**9**
5	Dissemination of harmful gases into the environment of the excavation truck	4	2	8	**4**									1	2	2	**6**	1	2	2	**3**	12	10	2,36	**10**
6	Wastewater in construction field					2	3	6	**4**	3	4	12	**1**	2	3	6	**3**	1	3	3	**2**	27	4	4,66	**8**
7	Emission of particulate matter consisting of sand, cement, lime, etc.	3	4	12	**2**	2	2	4	**5**	1	2	2	**4**	1	2	2	**6**	2	2	4	**1**	24	6	5,45	**5**
8	Dust formation during destruction of constructions	4	4	16	**1**	1	3	3	**6**					2	2	4	**4**	1	2	2	**3**	25	5	5,92	**4**
9	Use of chemical components contained in building materials	2	4	8	**4**	2	2	4	**5**	2	2	4	**3**	1	3	3	**5**	1	2	2	**3**	21	7	4,59	**7**
10	Fire due to flammable insulating materials	2	3	6	**5**	2	3	6	**4**	1	2	2	**4**	2	2	4	**4**	1	2	2	**3**	20	8	5,08	**6**
		Total		64	2	**Total**		66	1	**Total**		36	5	**Total**		52	3	**Total**						37	4
		Weighted Total		14.96	2	**Weighted Total**		30.46	1	**Weighted Total**		2.08	5	**Weighted Total**		7.83	3	**Weighted Total**						3.57	4

According to the L Type risk assessment results, having a narrow range of occurrence and severity parameters lead to occupational health and safety specialists hesitant. Hence, Fuzzy evaluation for scoring risks has been proposed in this study.

Calculate Fuzzy RPN for Each Danger

For O, S and RPN values, fuzzy membership functions from Tables 4 and 5 are taken into consideration respectively and coded by using the Fuzzy Logic Designer Tool in Matlab. O and S parameters are used as inputs, and the RPN is the output. The fuzzy design developed in this study is provided in Figure 2. As demonstrated in Figure 2, the 'Mamdani min-max' method is used.

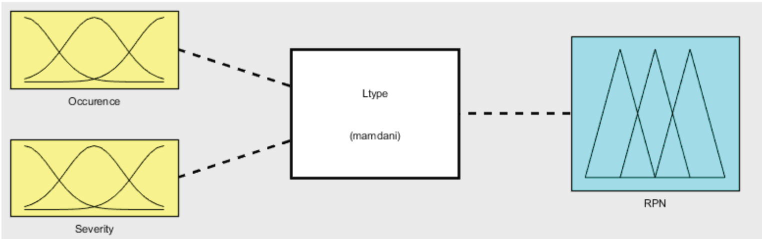

Figure 2. Design of Fuzzy L-Type

Five levels of O and S parameters are taken into consideration and 25 decision rules have been formed. According to the decision rules, fuzzy L Type RPN values of environmental risks for construction activities are calculated and presented in Table 8. "Dust formation during destruction of constructions"; "Leaving construction and demolition waste to the agricultural fields"; "Wastewater in construction field"; "Mass Wasting" is obtained as the most important risks for the air, soil, water, and flora impact categories respectively according to the fuzzy approach. "Mass Wasting" and "Contamination of paint residues to soil" are the most important risks according to the total risk score similar to classic approach results. In contrary to the classic approach, the third most important risk is found as "Wastewater in construction field" with a fuzzy approach. Similar to the previous calculations, weighted total risk scores are calculated for the same risks in the fuzzy approach. According to the results; "Leaving construction and demolition waste to the agricultural fields" is determined as the most important risk followed by "Mass Wasting" and "Contamination of paint residues to soil".

In Table 8, environmental impact scores are assessed as well. Total impact scores are calculated as 86.09; 89.09; 48.78; 67.74; 24.88 for air, soil, water, flora, and fauna respectively according to the sum of all defined fuzzy risk scores. In addition to that, weighted total fuzzy impact scores are calculated and scores of 20.12; 41.48; 2.82; 10.20 and 2.40 for air, soil, water, flora, and fauna are found respectively. These fuzzy impact scores present that, soil and air are the most affected impact categories due to construction activities.

Comparison of Classic and Fuzzy RPN

In Table 9, the ranks of risks according to classic and fuzzy approaches are compared. In fuzzy L Type risk assessment;

- In the "Air" impact category; risk levels of 5 out of 8 risks have increased, 3 of them remained the same.
- In the "Soil" impact category, risk levels of 6 out of 8 risks have increased, 2 of them remained the same.
- In "Water" impact category risk levels of all risks remained the same at the same level.
- In the "Flora" impact category; risk levels of 2 out of 10 risks have increased; 5 of them remained the same and 3 of them decreased due to a decrease in the risk score.
- In the "Fauna" impact category; risk levels of 7 out of 10 risks have increased; 3 of them remained the same.
- For each risk, according to total risk scores, risk levels of 2 out of 10 risks have increased, 5 of them remained the same.
- For each risk, according to weighted total risk scores, 3 out of 10 risks have increased and 3 of them remained the same.
-

Table 8. Fuzzy L-type risk scores and priorities

Risk #	Risks	Air		Soil		Water		Flora		Fauna		Total Risk Score	Rank	Weighted Total Risk Score	Rank
		0,233736		0,461477		0,057815		0,150618		0,096354					
		RPN	Rank	RPN	Rank	RPN	Rank	RPN	Rank	RPN	Rank				
1	Mass Wasting			17	2	10,3	2	17	1	4,33	1	48,63	1	11,42	2
2	Contamination of paint residues to soil	4,33	4	17	2	10,3	2	10,3	2	1,26	2	43,19	2	11,13	3
3	Leaving construction and demolition waste to the agricultural fields	1,26	5	22,3	1	4,33	3	10,3	2	1,26	2	39,45	4	12,51	1
4	Dissemination of harmful gases into the environment in the excavation process	10,3	3					4,33	3	4,33	1	18,96	9	3,48	9
5	Dissemination of harmful gases into the environment of the excavation truck	10,3	3					1,26	4	1,26	2	12,82	10	2,72	10
6	Wastewater in construction field			10,3	3	17	1	10,3	2	4,33	1	41,93	3	7,70	6
7	Emission of particulate matter consisting of sand, cement, lime, etc.	17	2	4,33	4	1,26	4	1,26	4	4,33	1	28,18	6	6,65	7
8	Dust formation during destruction of constructions	22,3	1	4,33	4			4,33	3	1,26	2	32,22	5	7,98	5
9	Use of chemical components contained in building materials	10,3	3	4,33	4	4,33	3	4,33	3	1,26	2	24,55	8	5,43	8
10	Fire due to flammable insulating materials	10,3	3	10,3	3	1,26	4	4,33	3	1,26	2	27,45	7	8,01	4
	Total	86,09	2	89,89	1	48,78	4	67,74	3	24,88	5				
	Weighted Total	20,12	2	41,48	1	2,82	4	10,20	3	2,40	5				

Table 9. Comparisons of priority orders

	Air		Soil		Water		Flora		Fauna		Total Risk Score		Weighted Total Risk Score	
Risk #	Classic Rank	Fuzzy Rank	Classic Rank	Fuzzy Rank	Classic Rank	Fuzzy Rank	Classic Rank	Fuzzy Rank	Classic Rank	Fuzzy Rank	Classic Rank	Fuzzy Rank	Classic Rank	Fuzzy Rank
1			2	2	2	2	1	1	1	1	1	1	1	2
2	6	4	3	2	2	2	3	2	3	2	2	2	3	3
3	7	5	1	1	3	3	3	2	3	2	3	4	2	1
4	3	3					1	3	1	1	9	9	9	9
5	4	3					3	4	3	2	10	10	10	10
6			4	3	1	1	2	2	2	1	4	3	8	6
7	2	2	5	4	4	4	1	4	1	1	6	6	5	7
8	1	1	6	4			3	3	3	2	5	5	4	5
9	4	3	5	4	3	3	3	3	3	2	7	8	7	8
10	5	3	4	3	4	4	3	3	3	2	8	7	6	4

In Table 9, when ranks of weighted total risk score and total risk scores are compared according to the classic approach, risk levels of 4 out of 10 risks have increased, 2 of them remained at the same level. However, when ranks of weighted total risk score and total risk scores are compared according to the fuzzy approach, risk levels of 2 out of 10 risks have increased and 4 of them remained at the same level. In all assessments, "Dissemination of harmful gases into the environment of the excavation truck" and "Wastewater in construction field" have placed as last.

In risk assessment studies, risks can be compared according to their risk levels instead of priority orders. Classic L-Type risk assessment levels are presented in Table 3. According to this table, risks that have an RPN value of 25 and more considered as "Unacceptable Risks". If RPN value decreases, risks become more acceptable. In Fuzzy L Type Risk assessment, RPN values are assessed according to their membership functions which are presented in Table 5. In the fuzzy approach, minimum and maximum values of class intervals coincide, hence fuzzy RPN value can be placed in two classes. Comparative risk classes are presented ina confusion matrix in Table 10 according to the impact categories

In Table 10, comparisons of classes of classic and fuzzy approaches are presented;

- In “Air” impact category; the level of risk classes of 3 out of 8 risks have increased
- In “Soil” impact category, level of risk classes of 4 out of 8 risks have increased
- In “Water” impact category; the level of risk classes of 3 out of 7 risks have increased
- In “Flora” impact category; the level of risk classes of 3 out of 10 risks have increased
- In the "Fauna" impact category; levels of risk classes of 4 out of 10 risks have remained the same class, while the rest of the classes is decreased.

Table 10. Confusion Matrix of Risk Classes

		Fuzzy																												
		Air						Soil					Water						Flora						Fauna					
		1	1-2	2	3	4	5	1	2	3	4	5	1	1-2	2	3	4	5	1	1-2	2	3	4	5	1	1-2	2	3	4	5
Classic	1																													
	2		1	1	1				3	2				2	2	2				2	4	2				6	4			
	3				3	1					1							1				1		1						
	4						1				1	1																		
	5																													

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Chapter 2

RECENT STUDIES ON DRYING METHODS AND EFFECTS OF DRYING METHODS ON PRODUCT QUALITY IN HERBS: MATHEMATICAL MODELS IN THE DRYING KINETICS

İbrahim Metin HASDEMİR[1]

Belma HASDEMİR[2]

1 Istanbul University-Cerrahpaşa, Engineering Faculty, Chemical Eng. Dept., 34320 Avcılar-İstanbul/TURKEY, E-mail: hasdemir@istanbul.edu.tr

2 Istanbul University-Cerrahpaşa, Engineering Faculty, Chemistry Dept., 34320 Avcılar-İstanbul/TURKEY, E-mail: karaefe@istanbul.edu.tr

Aromatic herbs are widely used for flavoring food and protecting human health in the food and medicine industry. Besides, they have a wide range of uses as nutritional supplements, herbal tea, taste, and fragrance. In recent years, the importance of medicinal and aromatic herbs has increased as a result of the diversity of human needs and the increase in demand for natural products. Moreover, essential oils obtained from herbs have taken their place as a big market in the world as an important input of the perfumery and cosmetics industry. The high economic value of essential oils and their wide range of use has led to an increase in interest in these herbs, to examine their chemical structures, and to investigate their biological activities in recent years. (Samarth et al., 2017; Inoue et al., 2019; Boukhatem et al., 2020; Ganaie, 2021). Bioactive compounds determine the quality of dried herbs. Essential oils obtained from herbs show Antimicrobial Activity against microorganisms (Qadir et al., 2017; Dai, et al., 2020; Hammamia, et al., 2020). Herbs degrade quickly as they have high humidity, therefore they must be processed immediately after harvest. The drying process protects the quality of the herb by reducing its moisture and inhibits the increase in biological deterioration. Therefore, it is very important to choose of drying method and suitable conditions. In recent decades, a large number of drying methods were investigated and dried herbs evaluated in terms of physical-chemical and biochemical changes (Ghafoora, et al., 2020; Gulati, et al., 2020). Besides, drying methods were examined kinetically in terms of moisture change and drying time. The most suitable drying conditions for foodstuffs are determined by mathematical models (Verboloz, et al., 2020; Gibson, et al., 2020).

This review is a survey of recent developments in drying methods of herbs and the impact of these methods on the physical-chemical and biological properties of the dried herbs. In addition to the study, mathematical models used in drying kinetics were reviewed too.

Drying methods

Drying or dehydration is one of the oldest and traditional food protection methods and there are many studies on the drying method in the literature. In these studies, it was stated that the drying method and the parameters applied has a significant effect on the phytochemical and antioxidant properties of dried herbs (Nguyen et al., 2018; Papoutsis et al., 2017; Vu et al., 2017; Shravya et al., 2019; Xua et al., 2020; Homayounfar et al., 2020).

Figure 1. shows the classification of drying methods commonly used in recent years.

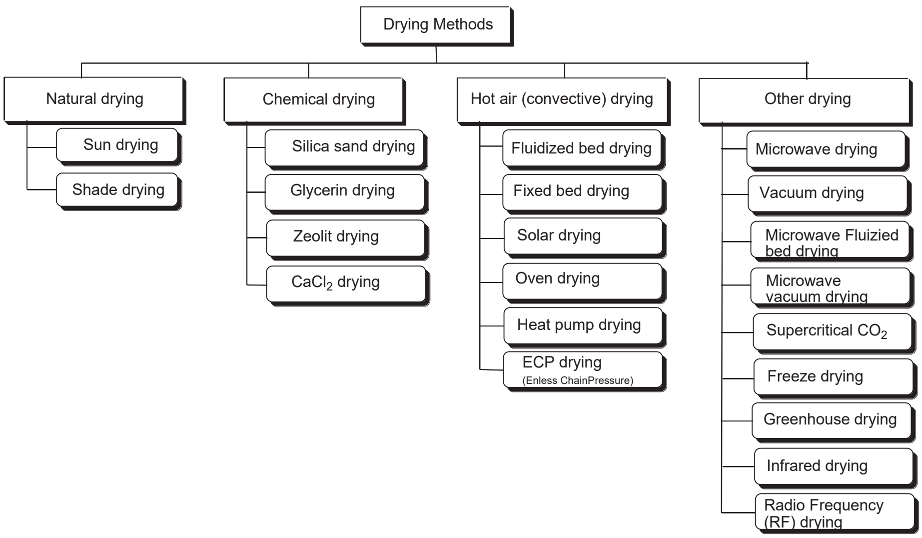

Figure 1. The classification of drying methods

Nowadays, the drying techniques commonly used for dried herbs are as follows:

Shade drying

In the shade drying process, herbs are located in a room that has sufficient airing, low moisture, and no direct exposure to sunlight. During drying, the material should be turned over frequently to prevent mold or rotting and to accelerate drying. Plants such as leaves and flowers that easily lose water and deteriorate at high temperatures can be dried well by the shade drying method. However, in this method, the drying time is much longer compared to sun drying (Mokhtarian et al.,2020).

Sun Drying

Although sun drying is a widely used the oldest natural drying method for medicinal and aromatic plants, it also brings many problems especially lower product quality. This method may not be a proper drying method for some plant species as it causes significant color and fragrance deterioration in dried herbs. The fact that the sun drying method takes a long time has led to the emergence of different drying methods that are healthier, faster, and more homogeneous on an industrial scale (Alara et al., 2018).

Hot-Air (Convective)Drying

Hot air drying of medicinal and aromatic herbs using convection ovens is still widely used today. The heat required to eradicate the moisture contained in the product is provided with the help of air and the evaporated moisture is removed from the product by air. Heat and moisture transfer occurs simultaneously between the product and the air, thus reducing the humidity of the product. Hot air drying systems have a simple design. The low operating and maintenance costs of these systems and the fact that different products can be dried according to the season can be counted among the advantages of these drying systems. Besides, The controllability of the parameters like airspeed, temperature, and drying time presents a prominent advantage for food producers in the industry (Ashtiani et al. 2017; Liang et al., 2020; Kiss et al., 2020).

Freeze Drying

The freeze-drying method has been used with several herbs. Control of heat conduction rate is very important in this technology. Since the frozen foodstuff should not melt, the heat transfer rate should be low enough to prevent the melting of ice. At the same time, to complete the drying within a short time, the heat conduction rate must be high. Essentially, freeze-drying can be evaluated to preserve the content of herbs more appropriately in comparison to drying methods that use heating.

This method can be used in the production of pharmacological products, fruit juices, coffee, and tea extracts, vegetable, meat, and milk production. However, the fact that the freezing technique is an expensive method has reduced its use (Jimenez-Garcia et al., 2020; Shonte et al., 2020).

Microwave Drying

Microwave drying reduces energy consumption during the drying process by allowing rapid evaporation of water from food. With this method, fruits and most food items with high initial moisture content are successfully dried. More suitable colors, more limited shrinkage, and rehydration capacity were noted in microwave dried products in comparison to hot air drying (Khodifad et al., 2020; Saeidi et al., 2020).

Vacuum Microwave Drying

Vacuum microwave drying, a modern drying technique, is widely used to improve the quality of dried products. The coupling of vacuum and microwave drying is submitted for drying herbs. In the microwave vacuum technique, the water content of herbs is eliminate using large condensers and vacuum pumps. Therefore, this method is proposed to be used in the later drying stage. However, system costs are more expensive because this method needs other drying steps and additional research (Calín-Sánchez et al., 2020).

Infrared Drying

In the infrared drying method, the heat required for the drying of foodstuffs is provided by infrared energy. Fast-drying, heating, and significant energy savings are among the advantages of the infrared drying method. Besides, during the drying of foodstuffs with this method, care should be taken to protect the color and nutrient content of the product as well as the drying efficiency (Ashtiani et al. 2017; Saeidi et al., 2020).

Over the last few years, various studies have been carried out on phenolic compounds, antioxidant activity, biological activity, color, and essential oil content of dried herbs using different drying methods and conditions. The latest researches are summarized in Table 1.

Rababah et al. dried four different herb species (sage, thyme, mint, and lemon balm) with air drying technic and studied the effect of the drying process on the total phenolics, antioxidant activity, flavonoid contents, and color properties. As a result of the investigation, they presented that air drying is a better method of drying than oven drying in terms of preserving photochemical contents (Rababah et al., 2015).

Ebadi et al. evaluated the influence of freeze, shade, oven, and vacuum drying methods on the essential oil composition of *Lippia citriodora* Kunth. They reported that vacuum drying with the 60 °C temperature looks to be an effective method for the casing of total essential oil content (Ebadi et al., 2015).

In another study, Siti Zulaikha et al. investigated the antioxidant activity and α-glucosidase inhibitory changes of the Phyllanthus acidus plant using oven, air, and freeze-drying techniques. According to the results of the study, they reported that the best antioxidant activity and α-glucosidase inhibitory were detected by 50% ethanolic extract of oven drying sample (Siti-Zulaikha et al., 2017).

In a review by Babu et al., researchers discussed the various drying methods for drying leaves and determined the suitable conditions to obtain more appropriate drying quality. Besides, they presented convenient mathematical models for measuring the moisture ratio (Babu et al., 2018).

In a review by Chua et al., the researchers mentioned a detailed study on the impact of the existing drying process on the essential oil content of various herbs as well as their antibacterial and antioxidant properties. As a result of the study, it was reported that no single method is effective for the dehydration of plants, and that heat treatment may lead to biochemical changes that increase antibacterial activity (Chua et al., 2019).

Fu and colleagues utilized to freeze, hot-air, vacuum, and microwave drying techniques to dry loquat leaves. They reported that different drying techniques can be effective on the physicochemical structures and bioactivities. They suggested that microwave drying could be an effective drying method. (Fu et al., 2020).

Thamkaew and colleagues, in their review articles, reported that drying techniques had an important effect on the physical properties (fragrance and color) and quality of dried herbs. They also reported several drying methods including supercritical carbon dioxide drying and heat-pump-assisted drying (Thamkaew et al., 2020).

Sánchez and colleagues, in their review article, compared with the traditional and novel drying techniques and also, reported the flaws of standard drying methods. They reported that freeze-drying is one of the most advised methods for protecting quality. However, they mentioned that one disadvantage of this method is that the product can lose flexibility and become viscous during rehydrating (Calín-Sánchez et al., 2020).

Setiaboma et al. investigated that the effect of different drying methods i.e. sun, shade, and cabinet drying on the physical and chemical properties of the herb (*Moringa oleifera*). They found that the sun drying method provided the highest minerals contents and antioxidant activity (Setiaboma et al., 2019).

Saifullah et al. evaluated the effects of different drying methods on phenolic content and antioxidant activity of lemon myrtle leaves and the most suitable drying conditions were identified. The results showed that drying conditions significantly affected the properties of lemon myrtle leaves. They reported that the freeze-drying method has the highest energy consumption, although it is the most effective method to preserve phytochemical and antioxidant properties (Saifullah et al., 2019).

Sadowska et al. investigated the effects of drying methods on antioxidant activity and the essential oil content of thyme and sage. For this purpose, The herbs collected were dried with natural (at the temperature of 35 - 40 °C) and freeze-drying techniques. The results obtained were discussed. The highest content of polyphenols for thyme was found by the natural drying method at 35 °C (Sadowska et al., 2017).

In another study, green tea was dried using different drying methods (sun, shade, oven, microwave, and freeze-drying), and these drying methods were evaluated for total flavonoid, phenolic, antioxidant activity, and vitamin C. They reported that the highest vitamin C and Chlorophyll-a were obtained in freeze drying (Roshanak et al., 2016).

Santana and co-workers discussed the influence of air-drying, convection oven, and solar drying on the physical and chemical properties of Ilex guayusa leaves. They reported that leaves showed the highest caffeine content and the lowest drying time when dried by a convection oven (Santana et al., 2018).

In a paper by Badee et al., it was reported that the effect of different drying methods on biological activities and chemical composition of parsley grass was examined and the results obtained are evaluated. According to their study results, they reported that oven drying slightly reduced oil yield compared to solar drying (Badee et al., 2020).

Turgay et al. studied the effect of drying methods on total phenolic content, antioxidant activity, ascorbic acid content, and color of *Ocimum bacilicum* L. from Turkey. The results of the study showed that antioxidant activity was increased in the dried herb, but thermal drying caused the discoloration in the plant and degradation in ascorbic acid (Turgay et al., 2020).

In the study by Mavrianingtyas et al., the researchers examined the effect of drying methods such as oven, sun, room temperature, and roasting on Moringa oleifera leaf. Besides, the level of total flavonoid and antioxidant capacity of the dried herb was measured. The highest total flavonoids and antioxidant capacity were achieved by the oven drying method (Mavrianingtyas et al., 2020).

Eneighe and co-workers were produced green tea from the leaves of *Xymalos monospora*using three different drying techniques (shade, sun, and oven drying). The total phenolic content of teas obtained by these drying methods was determined, drying kinetics were examined. The results showed that the Modified Page equation is the best equation to describe the drying kinetics. Activation energy is determined as 27.89 kJ/mol. The oven-drying (60 °C) was recommended for the best total polyphenol, proteins, and fiber content is recommended (Eneighe et al., 2020).

Mustafa et al. reported that the effect of different drying techniques (shade, sun, and oven drying) was investigated on drying kinetics, color, and antioxidant activity of Artocarpus heterophyllus Lam. The results showed that shade drying could be able to protect color better than oven and sun drying methods and the Newton model was the best fitted mathematical model for drying kinetics (Mustafa et al., 2020).

In the study by Salve et al., Mentha spicata leaves were dried by the sun (30 - 35°C), shade (27 - 32 °C), and oven (60 °C) drying methods and the results were evaluated in terms of chemical composition, nutritional and phytochemical properties. The results demonstrated that the quality of end dried products is superior as compared to dried products by other drying techniques, although energy consumption and time have taken more in the shade drying method (Salve et al., 2020).

In the other study, Mokhtarikhah et al., investigated shade, sun, vacuum, microwave, oven, freeze-drying, and infrared methods on the spearmint essential oil quality. They reported that shade and oven-drying with the temperature 60 °C and 40 °C prescribed methods for *Mentha spicata* L. (Mokhtarikhah et al.,2020).

Sibero et al. studied the effect of oven and sun drying methods on the metabolite profile of R. apiculataleaves. They found that there were no differences in metabolites in dried and fresh R. Apiculata leaves (Sibero et al., 2020).

Saeidi and colleagues reported that Hyssop (*Hyssopus offisinalis* L.) dried by shade, sun, oven, microwave, and infrared drying methods and the effect of different drying methods on the drying time, essential oil content, and composition. The results showed that the use of the infrared drying technique for hyssop drying protected the quantity and quality of the active substances (Saeidi et al., 2020).

In the study by Jimenez-Garcia et al., melissa, peppermint, and thyme were dried using microwave, conventional and freeze-drying techniques. Then, phenolic compounds, antioxidant activity, and inhibitory enzymes in these herbs were determined. The study results indicated that the freeze-drying technique has high reliability, but this process is expensive and limited in its application (Jimenez-Garcia et al.,.2020).

Pandey and co-workers investigated the effects of shade and oven drying methods on the yield and quality of essential oil of patchouli herb. The results showed that the best essential oil yield was found in patchouli leaves oven dried at 40 °C (Pandey et al., 2020).

Homayounfar et al., studied the effect of different drying methods on drying speed, color index, total phenol content, and antioxidant capacity during drying of Lavender leaves. They reported that a near infrared-vacuum dryer was the more suitable for drying lavender leaves (Homayounfar et al., 2020).

In the study by Khodja et al., Laurus nobilis leaves were dried with microwave-assisted drying and a conventional drying method and evaluated drying kinetics. Besides, the total phenolic content and antioxidant activity of the Laurus nobilis leaves were studied. Kinetic results showed that the microwave drying method is much more efficient compared to traditional drying methods. Moreover, The highest content of phenolic compounds and antioxidant activity was found using open-air and microwave drying methods (Khodja et al., 2020).

Gong and colleagues examined the impact of different drying techniques on phenolic composition and antioxidant activity of *Sedum aizoon* L. They reported that among the drying methods, the freeze-dried fraction exhibited the highest antioxidant activities and total flavonoids (Gond et al., 2020).

In the study by Monteiro et al., Pereskia aculeata Miller leaves were dried using air drying, freeze-drying, and microwave vacuum drying methods and evaluated the quality and physicochemical properties of the dried powdered leaves. The results indicated that microwave vacuum drying can be an appropriate alternative to traditional drying methods due to the higher drying rate and shorter drying time (Monteiro et al.,2020).

Muhammad et al. studied the effect of air, sun, and oven drying methods on *Ocimum gratissimum* leaf and evaluated the organic and dietary elemental composition of its leaves. The research revealed that the different drying method does not affect the level of nutrients (Muhammad et al., 2020).

Mohamad et al. used different drying methods (sun drying, vacuum oven drying, and freeze-drying) for drying ginger and determined the proximate composition, color analysis, and total phenolic content of its. They reported that freeze-dried ginger presents the best result for retaining nutrients, color, and total phenolic content (Mohamad et al., 2020).

Morshedloo and colleagues evaluated the effect of different drying methods i.e. shade drying, sun drying, oven drying, microwave drying, and freeze-drying methods on the essential oil content and compositions of Iranian dragonhead. They found that the highest essential oil contents were determined in the freeze-drying method despite the lowest essential oil contents were determined in the oven drying at 60 °C (Morshedloo et al., 2020).

In the study by Odunayo et al., researchers dried Coriander leaves using the oven drying method (at 40, 50, 60, and 70 °C) and studied how drying temperatures affected the moisture content of the leaves. Also, mathematical models were used to investigate the drying behavior and kinetics of the product. The results showed that increasing the drying temperature increased the amount of moisture removed from the leaves and the best model to describes the drying characteristics of Coriander leaves was Hii et al. model (Odunayo et al., 2020).

Morakinyo et al. focused on the drying kinetics of Ceratotheca sesamoides leaves and the determination of their mineral compositions. For this purpose, eight mathematical models (Page, Modified Page, Midili, Newton, Two-term, Henderson and Pabis, Logarithmic and Modified Henderson and Pabis) were used (Morakinyo et al.,2020).

Table 1. Various drying methods for herbs

Herb Material	Drying Method	Examined properties	Ref.
Ocimum bacilicum L.	Sun Microwave	Antioxidant activity Total phenolic content Ascorbic acid content Color	Turgay et al., 2020
Ocimum gratissimum	Air Sun Oven	Phytochemical and Some Nutrient Components	Muhammad et al., 2020

Parsley	Oven Solar	Chemical composition Biological activity	Badee et al., 2020
Moringa oleifera	Shade Sun Oven	Total flavonoid Antioxidant capacity	Mavrianingtyas et al., 2020
Xymalos monospora	Shade Sun Oven	Total phenolic content Drying kinetic	Eneighe et al., 2020
Artocarpus heterophyllus Lam.	Shade Sun Oven	Color Antioxidant properties Drying kinetic	Mustafa et al., 2020
Mentha spicata L.	Shade Sun Oven Microwave Freeze Infrared	Chemical composition Nutritional phytochemical properties Essential oil content	Salve et al., 2020 Mokhtarikhah et al., 2020
Mentha piperita L	Shade Sun Solar	Physicochemical properties	Mokhtarian et al., 2020
Rhizophora apiculata	Sun Oven	Effect on metabolite profile	Sibero et al., 2020
Hyssopus offisinalis L.	Shade Sun Oven Microwave İnfrared	Drying time Essential oil content and composition	Saeidi et al., 2020
Melissa, peppermint, thyme, mint	Microwave Conventional Freeze	Phenolic compounds Antioxidant activity Inhibitory enzymes	Jimenez-Garcia et al., 2020

Table 1. (continued)

Herb Material	**Drying Method**	**Examined properties**	**Ref.**
Pogostemon cablin (Patchouli)	Shade Oven	Essential oil content	Pandey et al., 2020
Lavender leaves	Atmospheric freeze Near infrared-vacuum	Drying speed Color index Total phenol content Antioxidant capacity	Homayounfar et al., 2020
Laurus nobilis L.	Microwave Open-air	Total phenolic content Antioxidant capacity	Khodja et al., 2020

	Oven		
Sedum aizoon L.	Sun Oven Freeze	Phenolic composition Antioxidant activity	Gong et al., 2020
Pereskia aculeata Miller	Air Freeze Microwave Vacuum	Physicochemical properties	Monteiro et al., 2020
Hyssopus offisinalis L.	Shade Sun Oven Microwave İnfrared	Drying time Essential oil content and composition	Saeidi et al., 2020
Zingiber officinale	Sun Vacuum oven Freeze	Composition Colour analysis Total phenolic content	Mohamad et al., 2020
Dracocephalum moldavica L.	Shade Sun Oven Microwave Freeze	Essential oil content	Morshedloo., 2020
Coriandrum Sativum L.	Oven (40, 50, 60 and 70°C)	Moisture content	Odunayo et al., 2020
Ceratotheca sesamoides	Oven (50, 60 and 70 °C)	Mineral compositions	Morakinyo et al., 2020
Murraya koenigii Leaves	Hot air Microwave-vacuum Freeze	Total phenolic content Antioxidant capasity Colour Water activity	Choo et al., 2020

Drying Kinetics

Studies drying kinetics is important to analyzing the drying behavior of a product. The drying kinetics could be interpreted using the drying curve and drying rate curve. The drying curve was obtained from the variation of moisture ratio (MR) as a function of time (t).

Moisture ratio is defined as follows (Eq.1) (Nguyen et al., 2019; Karimi et al., 2021)

$$MR = \frac{M_t - M_e}{M_0 - M_e} \quad (1)$$

Where
MR: moisture ratio (dimensionless)
M_t : moisture content at t (kg water/kg dry solids),
M_0 : initial moisture content (kg water/dry solids)
M_e: equilibrium moisture content (kg water/dry solids)

Mathematical models used in drying processes are summarized in Table 2 (Ertekin et al., 2017; Alibas et al., 2020).

Table 2. Mathematical models used to the drying kinetics

Model Name	Equations
Aghbashlo et al.	$MR = \exp\left[-k_1 t/\left(1+k_2 t\right)\right]$
Alibas	$MR = a\exp\left[\left(-kt^n\right)+bt\right]+c$
Asymptotic	$MR = a_0 + a\exp(-kt)$
Chavez-Mendez et al.	$MR = a + b\ln(t)$
Demir et al.	$MR = a\exp\left[\left(-kt\right)^n\right]+b$
Diffusion approach	$MR = a\exp(-kt)+(1-a)\exp(-kbt)$
Geometric	$MR = at^{-n}$
Haghi and Angiz-I	$MR = a\exp\left(-bt^c\right)+dt^2+et+f$
Haghi and Angiz-II	$MR = a+bt+ct^2+dt^3$
Haghi and Angiz-III	$MR = \left(a+bt\right)/\left(1+ct+dt^2\right)$
Haghi and Angiz-IV	$MR = a\exp\left[\frac{-\left(t-b\right)^2}{2c^2}\right]$
Hasibuan and Daud	$MR = 1-at^n\exp\left(-kt^m\right)$
Henderson and Henderson I	$MR = c\left[\exp(-kt)+\frac{1}{9}\exp(-9kt)\right]$
Henderson and Henderson II	$MR = c\exp(-kt)+\frac{1}{9}\exp(-9kt)$
Henderson and Pabis	$MR = a\exp\left(-kt\right)$
Modified Henderson and Pabis I	$MR = a\exp\left(-k_0 t\right)+b\exp\left(-k_1 t\right)+c\exp\left(-ht\right)$

Modified Henderson and Pabis II	$MR = a\exp\left(-kt^n\right) + b\exp\left(-gt\right) + c\exp\left(-ht\right)$
Modified Henderson and Perry	$MR = a\exp(-kt^n)$
Hii et al.	$MR = a\exp\left(-kt^n\right) + c\exp\left(-gt^n\right)$
Jena and Das	$MR = a\exp\left(-kt + b\sqrt{t}\right) + c$
Lewis (Newton)	$MR = \exp\left(-kt\right)$
Logaritmic	$MR = a\exp\left(-kt\right) + c$

Table 2. (continued)

Model Name	**Equations**
Logistic	$MR = a_0 / \left[1 + a\exp(kt)\right]$
Midilli et al.	$MR = a\exp\left(-kt^n\right) + bt$
Modified Midilli et al-I	$MR = \exp\left(-kt^n\right) + bt$
Modified Midilli et al-II	$MR = \exp\left(-kt\right) + bt$
Modified Midilli et al-III	$MR = a\exp\left(-kt\right) + bt$
Noomhorm and Verma	$MR = a\exp(-kt) + b\exp(-gt) + c$
Otsura et al.	$MR = 1 - \exp\left[-\left(kt^n\right)\right]$
Page	$MR = \exp(-kt^n)$
Modified I	$MR = \exp\left[\left(-kt\right)^n\right]$
Modified II	$MR = \exp\left[-\left(kt\right)^n\right]$
Modified III	$MR = \exp\left[-\left(-kt\right)^n\right]$
Modified IV	$MR = a\exp\left[-\left(kt^n\right)\right]$
Modified V	$MR = \exp\left[-\left(kt^n\right)\right]$
Modified VI	$MR = \exp\left(kt^n\right)$
Modified VII	$MR = \exp\left[-k\left(t / L^2\right)^n\right]$
Modified VIII	$MR = \exp\left\{-\left[k\left(t / L^2\right)^n\right]\right\}$
Modified IX	$MR = k\exp\left[\left(-t / L^2\right)^n\right]$
Parabolic	$MR = a + bt + ct^2$
Power Law	$MR = at^b$

Regression -I	$MR = \exp\left[-\left(at^2 + bt\right)\right]$
Sharaf-Eldeen et al.	$MR = a\exp(kt) + \left[1 - a\exp(-bkt)\right]$
Simplified Fick's	$MR = k\exp\left[-c\left(t / L^2\right)\right]$
Sripinyowanich and Noomhorm	$MR = \exp\left(-kt^n\right) + bt + c$
Thompson	$MR = \exp\left\{\left[-a - \left(a^2 + 4bt\right)^{0.5} / 2b\right]\right\}$
Two Term	$MR = a\exp\left(-k_0 t\right) + b\exp\left(-k_1 t\right)$
Modified Two Term	$MR = a\exp\left(-k_0 t\right) + \left(1 - a\right)\exp\left(-k_1 t\right)$
Two-Term Exponential	$MR = a\exp\left(-kt\right) + \left(1 - a\right)\exp\left(-kat\right)$
Vega-Galvez et al.I	$MR = n + k\sqrt{t}$
Vega-Galvez et al.II	$MR = \exp\left(n + kt\right)$
Vega-Galvez et al.III	$MR = \left(a + bt\right)^2$
Verma et al.	$MR = a\exp\left(-kt\right) + \left(1 - a\right)\exp\left(-gt\right)$

Table 2. (continued)

Model Name	Equations
Wang et al. I	$MR = a\exp\left(bkt\right) + \left(1 - a\right)$
Wang et al.II	$MR = \left(1 - a\right)\exp(bkt) + a\exp(ckt)$
Wang et al.III	$MR = \left(1 - a - b\right)\exp(ckt) + a\exp(dkt) + b\exp\left(fkt\right)$
Wang and Singh	$MR = 1 + at + bt^2$
Weibull Distribution-I	$MR = a - b\exp\left[-\left(kt^n\right)\right]$

MR, moisture ratio; a, b, c, d, f, g, h, coefficients; t, drying period, min; n, drying constant; k, k_0, k_1, k_2, special drying constant, min^{-1};
L, thickness of material (mm).

There were three evaluation criteria in determining the appropriate drying mathematical model. These are coefficient of determination (R^2), root mean square error (RMSE) and chi-squared (χ^2). They calculated according to Eqs. (2), (3) and (4). The higher R^2 value (closer to one) and lower χ^2 and RMSE values (closer to zero) represent the best model (Nguyen et al., 2019; Karimi et al., 2021).

$$R^2 = 1 - \frac{\sum_{i=1}^{N}\left(MR_{\mathrm{exp,i}} - MR_{\mathrm{pre,i}}\right)^2}{\sum_{i=1}^{N}\left(\overline{MR_{\mathrm{exp,i}}} - MR_{\mathrm{pre,i}}\right)^2} \tag{2}$$

$$RMSE = \sqrt{\frac{1}{N}\left(MR_{\mathrm{exp,i}} - MR_{\mathrm{pre,i}}\right)^2} \tag{3}$$

$$\chi^2 = \frac{\sum_{i=1}^{N}\left(MR_{\mathrm{exp,i}} - MR_{\mathrm{pre,i}}\right)^2}{N - Z} \tag{4}$$

where
$MR_{exp,i}$: experimental moisture ratio (dimensionless)
$MR_{pre,i}$: predicted moisture ratio (dimensionless)
N : number of observations
Z : constant

The moisture diffusion of herbs is calculated with the equations given below based on Fick's second diffusion equation (Eq.5).

$$\frac{\partial M}{\partial t} = D_{eff}\frac{\partial^2 M}{\partial x^2} \tag{5}$$

$$MR = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{\left(2n+1\right)^2}\exp\left(-\left(2n+1\right)^2\pi^2\frac{D_{eff}}{4L^2}t\right) \tag{6}$$

$$\ln(MR) = \ln\left(\frac{8}{\pi^2}\right) - \left(\pi^2 \frac{D_{eff}}{4L^2} t\right) \quad (7)$$

where

MR : moisture ratio (dimensionless)
L : half-thickness (m)
n : term in series expansion
t : time

The value of the effective diffusion coefficient is calculated from the slope of the line obtained by plotting ln (MR) values versus time (*t*). As can be seen from Equation 7, the graph drawn gives a line with a slope of $-\pi^2 D_{eff} / 4L^2$

The change of effective diffusion coefficient with temperatureis calculated by the Arrhenius equation (Eq.8)

$$D_{eff} = D_0 \exp\left(-\frac{E_a}{RT}\right) \quad (8)$$

where
D_{eff} : effective diffusion coefficient (m^2/s)
D_0 : pre-exponential factor (m^2/s)
E_a : activation energy (kJ/mol)
R : ideal gas constant (8.3143 kJ/mol)
T : absolute temperature (K)

The various thin layer drying models used in drying processes of various herbs are summarized in Table 3.

Table 3. Drying kinetic models reported in literature, used for dried herbs.

Material	Drying Methods	Model	Best Model	Ref.
Purple basil leaves (*Ocimum basilicum* L.)	Sun Freeze Microwave Hot air-oven	Lewis, Page, Modified Page I, Henderson and Pabis, Modified Henderson and Pabis, Logarithmic, Midilli, Modified Midilli, Two-Term, Two-Term Exponential, Wang and Singh	Modified Henderson and Pabis, Page, Logarithmic,	Altay et al., 2019
Mint leaves	Hot air (45, 55, 65 °C)	Newton, Page, Logarithmic, Diffusion approach, Henderson and Pabis models	Diffusion approach, Henderson and Pabis	Raviteja et al., 2019

Table 3. (continued)

Material	Drying Methods	Model	Best Model	Ref.
Mint leaves	Heatless Pressure Swing Adsorption (PSA)	Newton, Page, Henderson Pabis, Logarithmic, Two Term, Two Term Exponential Diffusion approach, Midilli et al. Wang and Singh	Midilli et al.	Venkatachalam et al., 2020
Clinacanthus	Heat pump,	Page	Midilli et al.	Norhaida et.al.,

nutans (*C. nutans*) leaves	(40, 50, 60 °C)	Henderson and Pabis Two term exponential Midilli et al.		2020
Corchorus olitorius, Crotalaria ochroleuca, Vigna unguiculata, Solanum villosum, Amaranthus blithum leaves	Hot air oven (30, 40, 50 °C)	Lewis, Page, Modified Page, Handerson and Pabis, Logaritmic, Two term, Two Term Exponential, Wang and Singh Verma et al., Mofied Page II, Midilli et all.	Modified Page	Mutuli et al., 2020
Coriander Leaves (*Coriandrum Sativum* L.)	Oven (40, 50, 60, 70 °C)	Lewis, Henderson and Pabis, Page, Verma et al., Logaritmic, Two Term, Diffusion approach, Midilli et al., Wang and Singh, Modified Page I, Mofified Page II, Modified Henderson Pabis , Hii et al.	Hii et al.	Odunayo et al., 2020
Lemon verbena leaves (*Lippia citriodora* Kunth)	Solar (30, 40, 50 °C)	Mofied Page, Lewis, Henderson and Pabis, Page, Verma et al., Logaritmic,	Midilli et al.	Moghaddam et al., 2020

		Two Term, Midilli et al. Wang and Singh, Diffusion approach		
Ceratotheca sesamoides leaves	Hot air oven (50, 60, 70 °C)	Page, Modified Page, Midili, Newton, Two-term, Henderson and Pabis, Logarithmic, Modified Henderson and Pabis	Page	Morakinyo et al., 2020
Fenugreek leaves (*Trigonella foenum-graecum L.*)	Hot air oven	Lewis, Herderson and Pabis, Page, Midilli et al. Logaritmic	Midilli et al.	Bishnoi et al., 2020

Table 3. (continued)

Material	Drying Methods	Model	Best Model	Ref.
Lettuce leaves	Solar	Newton, Page, Modified Page I, Henderson and Pabis, Modified Henderson and Pabis, Logaritmic, Midilli et. al., Verna, Wang and Singh, Thompson, Weibull Distribution, Two Term, Two Term Exponential, Diffusion approach	Page, Midilli et al, Weibull Distribution	Mezquita et al., 2020

Jackfruit leaves	Shade, Sun, Oven	Newton, Logarithmic, Verna, Two Term, Midlli, Page Henderson and Pabis	Newton	Mustafa et al., 2020
Ambang leaves	Sun, Shade, Oven	Newton, Page, Modified Page, Henderson and Pabis, Two Term Exponential, Logarithmic	Modified Page	Eneighe et al., 2020
Murraya koenigii Leaves	Hot air, Microwave-vacuum, Freeze	Lewis, Midilli-Kucuk, Modified Page	Lewis, Midilli-Kucuk, Modified Page	Choo et al., 2020

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Chapter 3

THE ROLE OF ANTIFOULING COATING IN THE MARINE INDUSTRY

Ayfer ERGİN[1]
M.Fatih ERGİN[2]

1 Asist. Prof. Dr. Ayfer ERGİN, İstanbul University-Cerrahpaşa, Engineering Faculty, Maritime Transportation Management Engineering ayfersan@istanbul.edu.tr
2 Dr.M.Fatih ERGİN, İstanbul University-Cerrahpaşa, Engineering Faculty, Chemistry Engineering mfergin@istanbul.edu.tr

1. Introduction

Marine biofouling can be described as the unwanted accumulation of plants, microorganisms, animals on surfaces immersed in sea water (ships, drilling rigs, mooring lines, etc.) (Hu, Xie, Ma, & Zhang, 2020). This case has been a trouble for the maritime industry for many years, and also has created many environmental and economic disadvantages. The fouling organisms easily stick to water-contact parts of ships, drilling rigs of petroleum, and breeding facilities (Dafforn, Lewis, & Johnston, 2011). Mussels and other invertebrates are held tightly to the hull surface by releasing a kind of bio-adhesive. As the mussels grow where they are held, the corrosion inhibitor layer on the hull will be damaged and then the hull corrosion will accelerate (Lejars, Margaillan, & Bressy, 2012).

These organisms will erode the hull surface and enhance the roughness of the hull (BARLAS, 2019; Dafforn et al., 2011; Y.-Q. Gu et al., 2015; Y. Gu et al., 2020; M. P. Schultz, 2007). As a result, fuel consumption and greenhouse gas emissions will rise (Dafforn et al., 2011; Dupraz et al., 2018; Feng et al., 2018; Y.-Q. Gu et al., 2015; Y. Gu et al., 2020; M. P. Schultz, 2007). Oil and natural gas exploration in the sea has developed rapidly in recent years. In addition to the shipping industry, fouling organisms cause serious damage to the drilling rigs. For example, drilling rigs in the open sea will be affected by fouling organisms and their weight will increase and then there's impact resistance will decrease against the waves they will encounter. Moreover, some invasive fouling organisms may be transported by ships moving between different regions, inducing the ecological balance to be disturbed (Miralles et al., 2016). Every year, large expenses are incurred for the hull cleaning, and maintenance of marine facilities. More than 80% of world trade is made by maritime transport (Yasa, Ergin, Ergin, & Alkan, 2016). Shipping trade was 4 billion tons in 1990, while it reached 11 billion tons in 2018 (UNCTAD, 2019). There has been a serious growth in world trade, especially in maritime transport, in the last 30 years. As the shipping industry grew, the damage caused by fouling organisms to the maritime economy has grown even more. The most effective and easy way to manage biological adhesion is to prevent the attachment from its source. The easiest and most common method to overcome this problem is antifouling coating (Y. Gu et al., 2020; Zhou, 2014). In conventional antifouling coatings, tin (Abbott, Abel, Arnold, & Milne, 2000; Maia et al., 2015) and copper oxide have frequently employed to remove contaminating organisms. Though copper oxide is less toxic than tin, its effect on marine ecology is gradually increasing as it continues to accumulate. Thus, the search for efficient and environmentally friendly antifouling coating has become an even more significant issue (Selim et al., 2015).

Studies on antifouling coatings, which are quite harmful to the environment, progress in two ways. One is to develop environmentally friendly and non-toxic antifouling materials instead of metal compounds, namely to obtain the antifouling active substances from the marine environment (Qian, Li, Xu, Li, & Fusetani, 2015; Satheesh, Ba-akdah, & Al-Sofyani, 2016). By purifying or modifying natural products by chemical methods, materials with extremely strong antifouling properties can be obtained. The second emphasizes antifouling coatings that will alter the surface properties of the material, make it hard for fouling organisms to adhere, or to facilitate removal after being added. Different fouling organisms, temperature, pH, salinity, such as reasons, it is very difficult for a single antifouling material to meet all requirements. For this reason, some composite antifouling coatings that combine multiple antifouling structures have also emerged. In addition, by the implementation of nanotechnology on different polymer materials today, the antifouling properties of the coating materials have been further enhanced (Z. Sun, Yang, Zhang, Bian, & Song, 2019).

2. Detrimental effects of fouling organisms on the maritime industry

Adhesion of fouling organisms to the water-contacting surfaces of the ships is undesirable. Although the fouling formation seems natural, it causes various harmful effects on the ship surfaces it is attached to. It has various detrimental impact such as the destruction of the surface to which it is attached, surface corrosion, increased fuel consumption, decreased maneuverability, increased release of greenhouse gases to the air, and the transport of invading species (Okay, 2004).

Fouling formation has many detrimental effects, but the most important are as follows;

- Fuel consumption
- Air pollution
- Transport of invasive species
- Destruction on the hull surface
- Hull maintenance
- The damages to underwater structures

2.1. Fuel consumption

Fouling organisms increases roughness of ship and therefore increases fuel consumption and emissions (M. E. Callow & Callow, 2002; Hu et al., 2020; Kowalski, 2020; M. Schultz, Bendick, Holm, & Hertel, 2011; M. P. Schultz, 2007; Stupak, García, & Pérez, 2003; Yebra, Kiil, & Dam-Johansen, 2004; Zhou, 2014). In addition, this situation reduces the maneuverability of the ship. (Stupak et al., 2003). The decrease in maneuverability causes an increase in fuel consumption and a loss of time in arrival and departure to the port. Fuel costs are 50-60% of operating costs (Corbett, Winebrake, Comer, & Green, 2011) and sometimes it can rise to 75% in a large container ship (Ronen, 2011).

As a result of biological contamination, it is either used with more power to maintain a certain speed, or it causes the speed to decrease when continuing at a certain power (Townsin, 2003). In the first case, there is higher fuel consumption. In the second case, the sailing time of the ship is extended, resulting in freight losses for ship owners. In both cases, it composes economic penalties. It has been observed that the weight of the adhering organisms per m^2 has reached 150 kg within a period of six months in ships that do not use any organic anti-adherence system today (Townsin, 2003). Fouling organisms induce deterioration of the hull surface and corrosion. As a result, the ship's weight increases and leads to a decrease in the cargo carrying capacity (Champ & Seligman, 1996; Damodaran et al., 1999; Hingston, Collins, Murphy, & Lester, 2001). Kawalski studied the effect of antifouling coating on fuel consumption over time in ro-ro ships. The study determined that a ship that did not employ antifouling coating for about 13 years caused an extra 2 tons of fuel consumption per day (Kowalski, 2020).

2.2. Air pollution

Maritime transport is the most environmentally friendly among other modes of transport (Ergin & Ergin), on the other hand, it accounts for 1.8% of the global greenhouse gases (Crippa et al., 2019). This is as much as the emission produced by a large country. This increase in fuel consumption caused by fouling organisms conducts an increase in the amount of CO_2, SO_2, NOx, etc. harmful gases released into the atmosphere. The amount of CO_2 generated by ships in 2019 is 714 million tons (IAE, 2020). It should be noted that the solvents contained in antifouling coatings used to prevent the accumulation of biological pollution are also released into the sea.

2.3. Transport of invasive species

Invasive microorganisms in the sea are species that have been transported from their natural habitat to another ecosystem. These can be transported by the fouling process. These invasive species cause the following adverse cases:

- The destruction or damage of organisms in the ecosystem they are transported to,
- The decrease in biological diversity,
- They can provide a medium for the transmission and spread of diseases. (Okay, 2004).

2.4. Destruction on the hull surface

Biofouling can cause corrosion of metal or concrete structures, block seawater pipelines of nuclear power plants, and impede nutrient exchange in aquaculture facilities (Hu et al., 2020). The fouling layer formed may induce thinning on the hull surface. Due to the wear of some places, it may lead to the surface of the hull weakening. Cleaning this layer formed on the surface of the hull gives rise to loss of time, cost, and work (freight loss). Interactions between metal, fouling, and seawater chemistry cause corrosion of metals in seawater. Fouling organisms can penetrate protective coatings and expose the underlying metal allowing subsequent corrosion to arise (Blackwood, Lim, Teo, Hu, & Pang, 2017).

2.5. Hull maintenance

Shipowners spend remarkable time reducing the effects of biofouling on ship performance. This causes ship owners to lose freight while dry-hull. The time to clean the hull surface may vary depending on the age of the ship. Generally, dry-hull can be done every 2½ to 3 years or every 5 years. Antifouling coating applications can modify according to ship type, speed, sailing time, trading areas, and geographic voyage pattern (Hellio & Yebra, 2009). Figure 1 shows the ship before and after dry-hull. During this process, large amounts of toxic waste are also generated (Yebra et al., 2004). The hull coating and hull surface roughness affect the ship's resistance. Hull roughness is generally estimated to be around 100-150 mm (SEEMP_FOR_CONTAINER_SHIP). Hull coating methods on ships can provide an average of 5% energy efficiency (Talay, Deniz, & Durmuşoğlu, 2014).

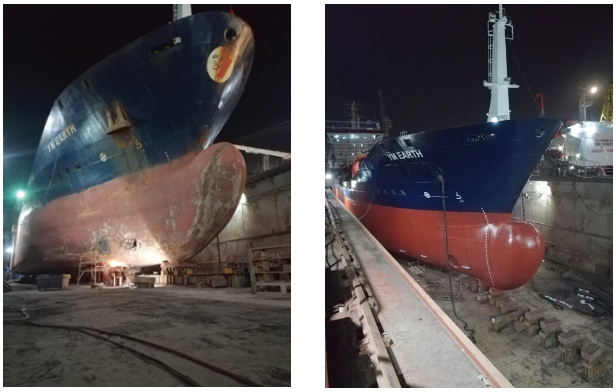


Figure 1: Ship before and after dry-hull.

Underwater hull cleaning extends the effective life of the antifouling coating and maintenance for longer dry-hull intervals. To maintain maximum performance and to extend the time between dry-hull, hull cleaning is carried out by professional divers. In Figure 2, it is seen that the hull surface is cleaned by divers (SEEMP_FOR_CONTAINER_SHIP). Adland et al expressed that dry-hull and hull cleaning reduced fuel consumption to between 9% and 17% (Adland, Cariou, Jia, & Wolff, 2018).

Figure 2: The hull surface is cleaned by divers.

2.6. The damages to underwater structures

Antifouling coatings are most utilized in oil and gas drilling rigs (Yebra et al., 2004) after ships. The fouling organisms adhere to drilling rigs over time, increasing the weight of these platforms. This situation increases the risks of the platforms against waves, storms, and tsunamis and causes a decrease in the usage time (Y. Gu et al., 2020). Another sector affected by fouling is aquaculture. Fouling in marine aquaculture is an important problem that induces increased operating costs and harmful effects on the cultivated species (Fitridge et al., 2012). In deep waters, fouling occurs more slowly. Moreover, it leads to problems in the long term in submarine structures (Hellio & Yebra, 2009).

3. Protection Methods from Biofouling

In order to prevent the living environments of the bio-fouling organisms attached to the ships and materials in the sea, to remove them and to prevent the expenses made, it is essential to know the fouling organisms that cause these formations.

It is very important to prevent surface damage caused by fouling organisms in the aquatic ecosystem. Various chemicals and many methods have been used to prevent this film formation. However, after many different methods that researchers have tried, it is the antifouling coating method that focuses on. The advantages of this method; It can be counted as not very costly in terms of cost, wide range of effects on fouling organisms, easy application, modification according to the environment used.

In order to better understand the biological fouling problem in the seas, it is necessary to know in detail how organisms adhere to the surfaces of materials and the adhesion mechanism. Biological fouling of the seas is a complex process in which biological communities accumulate on the material surface. Biofouling can be generally examined in three stages: conditioned film, microfouling, and macrofouling (see Figure 3).

- Conditioned film (Meseguer Yebra, Kiil, Weinell, & Dam-Johansen, 2006): When a clean surface is placed in sea water, many organic substances will accumulate on this surface in a short time and cause a thin film to form.

- Microfouling (Magin, Cooper, & Brennan, 2010; Rosenhahn, Schilp, Kreuzer, & Grunze, 2010): After the conditioned film is formed, bacteria, diatoms, and many organisms will be collected on the conditioned film. Biofilm created by these structures by secreting extracellular polymer structures (EPS) is called microfouling.

- Macrofouling (J. A. Callow & Callow, 2011): The resulting biofilms provide ample food for multicellular species and larvae of large marine organisms. Mussels, shellfish, and other large organisms attach to the surface and grow within a few days and macrofouling occurs.

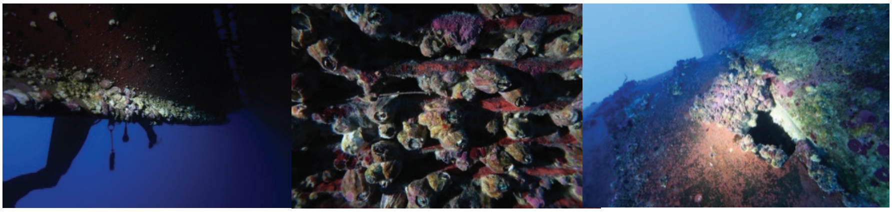


Figure 3: Fouling organisms on the surface of ships.

3.1. Use of Antifouling Coating

Antifouling coatings, in its simplest definition, are a kind of antifouling coating that prevents marine organisms from being removed from the surfaces and coated on the surfaces. Antifouling coating is used in many areas to control marine fouling. Shipping vessels come first with a rate of 43%. In recent years, oil and natural gas exploration activities in the seas have increased. Nowadays, after shipping vessels, antifouling materials the most employed in drilling rigs. Fishing boats, yachts & boats, morning lines, inland water transportation follow them, respectively (antifouling-coatings-market). Antifouling coatings basically realize protection method with two working principles. One of them aims to prevent the various groups in antifouling coating from dissolving in the sea and damaging the fouling organisms that want to hold on the surface. Another type of antifouling coating is to prevent fouling organisms from adhering by creating a slippery surface.

3.2. What Is Antifouling Coating?

Antifouling coatings are preferred due to their broad effects on contaminating organisms and protect the applied surfaces for many years even in a single application. However, intensive research has been carried out by many researchers for a long time in order to increase the duration of action of antifouling coatings and to minimize the damage they cause to the environment.

Antifouling coatings are coatings applied to vessels to prevent unwanted fouling organisms from adhering to the surface. These dyes are effective against shell and algae species that only target fouling.

It is important for the food chain that antifouling coatings do not harm beneficial organisms and food types. This feature of antifouling coatings is achieved with the active substance called "biocide". The European Union Commission defines the biocide as "The chemicals used to stop or suppress the damage of organisms that harm humans and animals or cause damage to natural or fabricated materials are called Biocides."

3.3. Antifouling Coating Types

Nowadays, antifouling coatings are generally developed on the basis of biocide or foul release. The post-application process of the antifouling coating applied to the surface of the ship is shown in Figure 4.

Biocide technology; it aims to prevent the formation of the fouling layer with chemicals, to transfer the chemicals to the sea water in a controlled manner and to prevent the adhesion or survival of the organisms approaching the ship surface.

Foul release technology; it aims not to use biocides, to use silicon-based polymers with a smooth surface and to use polymers with low surface energy.

Coatings produced with foul release technology are not preferred over biocide technology due to their high cost and short performance time.

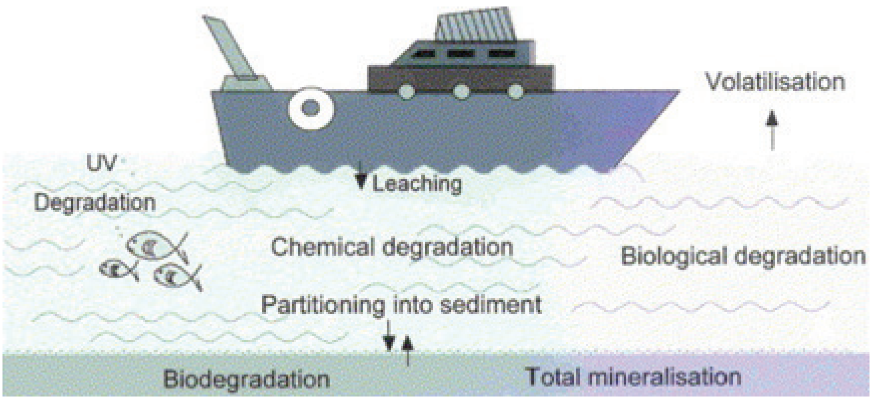


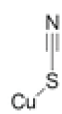
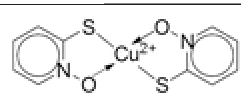
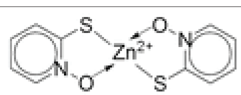
Figure 4: Movement of antifouling coatings in the marine environment (Almeida, Diamantino, & de Sousa, 2007).

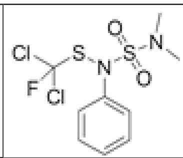
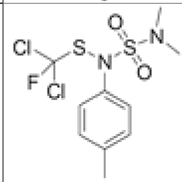
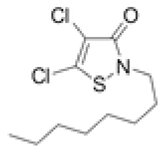
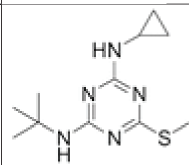
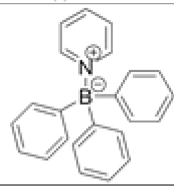
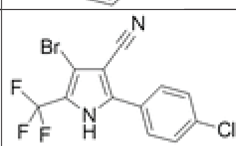
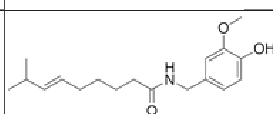
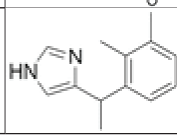
3.4. Antifouling Coating

With the development of the chemical industry in the 1960s, tributyl-tin (TBT) was discovered as a result of the investigation of metallic compounds for antifouling. Self-gloss copolymer-based coatings containing TBT are highly effective in preventing the settlement and growth of fouling organisms in the sea. It was determined that the half-life of TBT, whose research continued until the 1980s, is longer than 6 months. It has been determined that TBT detected in marine organisms near the surface is 1000 times higher compared to normal organisms. The fact that TBT is effective even at low concentrations in the sea is one of the most important reasons for its use. However, it has toxic effects on beneficial organisms as well as harmful effects extending to the food chain of humans. TBT can cause a variety of problems, from the deformation and thickening of the crustacean shell to the sex differentiation of some organisms, to the impairment of the immune systems of fish and marine mammals. TBT has been used in antifoiling coating since the 1960s (Lewis, 1998). While the lifetime of traditional antifouling coatings is 2 years, the lifetime of TBT is more than 5 years. Due to its negative effects on marine life over time, IMO (International Maritime Organization) banned the production of TBT and its application to ships on January 1, 2003. It has been forbidden TBT containing antifouling paints and coatings on the surface of the ships since January 1, 2008 (IMO, 2001).

After TBT-based products were banned in antifouling coatings, copper (Cu) based preservatives were used as an alternative. Copper structures, which are less toxic to the environment than TBT, have been reinforced with performance enhancers such as different cobiosides (Swain & Linings, 1999). Toxicity studies on biocides are continuing intensively. Sweden (Ytreberg, Karlsson, & Eklund, 2010) and US states Washington and California (Bill; Blossom, Szafranski, Yacht, & Lotz, 2018) made regulations regarding copper emission. Table 1 contains a list of currently used biocides and candidates. Studies have been conducted based on the mode of action, environmental permanence and toxicological properties of all these compounds (Arai, Harino, Ohji, & Langston, 2009; Hellio & Yebra, 2009; Konstantinou & Albanis, 2004; Omae, 2003; Thomas & Brooks, 2010; Voulvoulis, Scrimshaw, & Lester, 1999).

Table 1: Biocides Used in Antifouling Coatings.

Biocide	Alternative name	Formulation
copper		
dicopper oxide (cuprous oxide)		
copper thiocyanate		
bis(1-hydroxy-1H-pyridine-2-thionate-O,S) copper	copper pyrithione	
zinc complex of 2-mercaptopyridine-1-oxide	zinc pyrithione	

N-dichlorofluoromethylthio-N′,N′-dimethyl-N-phenylsulfamide	Dichlofluanid, Preventol A4S, Euparen	
N-dichlorofluoromethylthio-N′,N′-dimethyl-N-p-tolylsulfamide	Tolylfluanid, Preventol A5S Euparen M	
4,5-dichloro-2-n-octyl-4-isothazolin-3-one	Sea-Nine 211, Kathon 287T, Kathon 930, DCOIT	
zinc ethylene bisdithiocarbamate	Zineb	
N′-tert-butyl-N-cyclopropyl-6-(methylthio)-1,3,5-triazine-2,4-diamine	Irgarol 1051, Cybutryne	
triphenylboron pyridine complex	TPBP	
2-(p-chlorophenyl)-3-cyano-4-bromo-5-trifluoromethyl pyrrole	Tralopyril, Econea	
N-[(4-hydroxy-3-methoxyphenyl)methyl]-8-methylnon-6-enamide	Capsaicin	
4-[1-(2,3-dimethylphenyl) ethyl]-3H-imidazole	Medetomidine, Selektope	

It has become very important to develop environmentally friendly systems that do not harm living organisms and prevent biological fouling in the seas. Researchers are working to reduce or minimize the environmental damage of antifouling coatings, for this purpose antifouling coatings; Controlled depletion coatings (CDPs), tin-free self-polishing coatings (TF-SPCs) and hybrid systems are examined under three main headings.

3.5. Controlled depletion coatings (CDPs)

These coatings constitute the first generation of tin-free antifouling coatings. These dyes are fortified by resins synthesized to control the dissolution of the more durable and soluble binder of the binder resin to develop conventional soluble matrix dyes.

The working mechanism is considered to be similar to known resin-based coatings. In addition, erodible coatings have non-toxic, physically drying and seawater binding properties combined with the polymeric substance capable of controlling the speed of dissolution (erosion) mechanisms through physical process.

These tin-free products do not erode like TBT-based self-regenerating coatings. The disadvantage of their mechanism, which contains high copper and co-biocides, is its toxic effect on the environment. Antifouling coatings containing copper oxide are widely used in ships today. However, these coatings also have potential environmental risks. The increase in the amount of copper contained in copper oxide coatings in the ocean causes the death of seaweeds, which negatively affects the ecological balance. Therefore, the use of coatings containing copper oxide is limited and even its use is planned to be banned. Among the general characteristics of ablative (non-corrosive) coatings, it is less expensive than TBT-based self-regenerating coatings, and it can be protected for more than 3 years as it does not require roughness control and body coating (Almeida et al., 2007). Used in speedboats and small yachts with short travel times (Crisp, 1973).

3.6. Tin-free self-polishing coatings (TF-SPCs)

In this type of antifouling coating mechanism, the chemical showing biocide activity is generally provided with an acrylic resin. The biocide material is hydrolyzed by the effect of ions in sea water and separated from the resin in a controlled manner. Thanks to its excellent polishing properties, the separation layer (leach layer) formed by such coatings are very thin and its mechanism is 5 years. However, despite the high number of patents approved in this area until 1996, these groups are never as effective as TBT. This is because the hydrophilic/hydrophobic balance of the matrix is affected by the chemical structure of the pendant groups, changing the transition temperature, water absorption, and possible swelling of the polymers (Vallee-Rehel, Langlois, & Guerin, 1998).

Also, these dyes are more stable as they do not contain rosin and its derivatives. This is an important feature for the protective layer. These are generally based on co-biocides and copper acrylates. Zinc acrylate and its derivatives are also used.

Figure 5 shows the mechanism of ion exchange between water-soluble zinc carboxyl polymer salt and sodium ions in seawater. In Figure 6, the super-activated hydrolysis mechanism is given together with the retention and release system, which includes different stages. When these polymers interact with seawater, they act as a self-polishing system with controlled release of biocides (Vallee-Rehel et al., 1998).

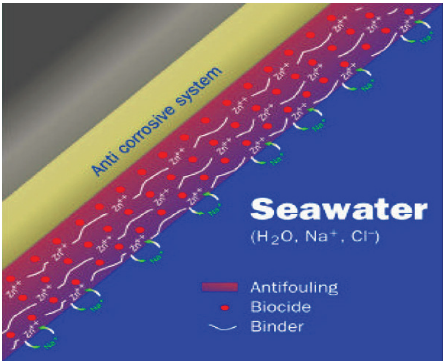


Figure 5: Tin-free self-polishing coatings release mechanism (Almeida et al., 2007).

The interaction of self-regenerating dyes containing antifouling biocide with sea water and the release of biocides into the marine ecosystem as a result of this interaction is shown in Figure 6.

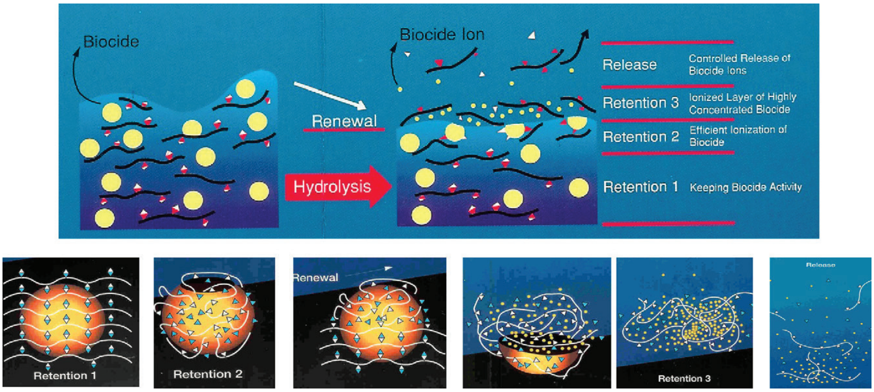


Figure 6: The release stages of biocides into the marine ecosystem (Almeida et al., 2007).

3.7. Hybrid systems

The mechanism of this dye system is much more complex than TF-CDP and SPC dyes, and it is a method under development recently. The homogeneity of the binder in the coating is achieved by using various cost-effective technologies such as nano-sized acrylates and microfibers. Hempel's Globic NCT is an example of this type of coatings. In addition to its high performance, its high cost has caused difficulties in choosing it (Swain & Linings, 1999).

3.8. Biocide-free coatings

De la Court and Vries (Almeida et al., 2007; TEN CENTS, 1973) predicted the development of low-energy non-polar coatings in order to prevent the adhesion of organisms to ship surfaces. However, these coatings were abandoned due to the problem of sticking to the surfaces of the ships.

However, the development of a biocide-free, inexpensive and environmentally friendly product has become very important today. These coatings differ from other coatings in that they move with a barrier layer and thus provide very low friction and have an ultra-smooth surface hydrophobically, so organisms cannot adhere to these coatings (Almeida et al., 2007; Baier, 1973; Dexter, 1976).

Any accumulation of organisms on the surface can be easily removed during the ship's motion, during the self-cleaning process or by a simple pressurized water jet (Swain & Linings, 1999).

These types of antifouling coatings are divided into two main categories: silicone and organic fluorine.

3.8.1. Organic Fluorine

The strong electronegativity, low polarizability and high C-F bond energy of fluorine atoms give polymers high stability, oleophobic and hydrophobic properties (Meiling et al., 2010). Arukalam et al. (Arukalam, Oguzie, Li, & science, 2016) prepared antifouling and corrosion inhibitor using poly (dimethylsiloxane) - ZnO (FDTS based PDMS-ZnO) nanocomposite coatings based on perfluorodesyltriclorosilane. ZnO has improved its adhesion by adding anti-bacterial ability to the coating and smoothness to the surface.

Xu et al. (Xu et al., 2017) prepared the polymer shown in Figure 7 using poly (ethylene glycol) (PEO) and poly (2,2,2-trifluoroethyl methacrylate) (PFMA) in their work. A self-cleaning surface has been formed by mixing the obtained polymeric structure with fluorine.

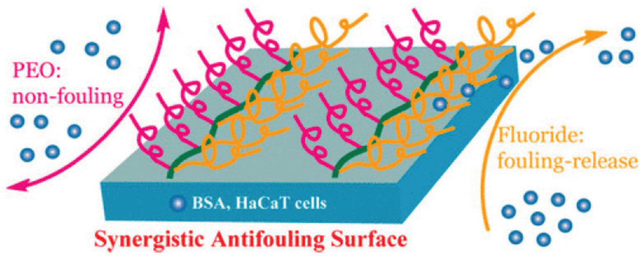


Figure 7: The synergistic antifouling surface.

3.8.2. Silicone

Nowadays, the high price of fluoropolymers and the problems in their preparation are difficult to achieve commercially, so silicone has become the preferred choice. Due to the good desorption properties of silicones, organisms can be easily cleaned on the surfaces they are applied to. Selim et al.(Selim et al., 2018) prepared a super hydrophobic PDMS-Ag® SiO2 core-shell nanocomposite antifouling coating using modified Stöber methods. Ag @ SiO2 core-shell nanophiles were placed on the surface of the PDMS material by solution casting method and a strong coating was formed according to the hydrazination curing mechanism.

3.9. Alternative Methods to Antifouling Coatings

There are some techniques used in the past years in order to remove the harmful layer formed by fouling organisms in the sea or to prevent them from living. Among these techniques, radiation, chemical, electrical, surface treatment and thermal techniques have been tested by Swain (Swain & Linings, 1999).

In a study, it was tested using ultrasonic vibration method to remove fouling organisms in the 1950s. In this system, as a result of the application of approximately 20 kHz ultrasonic frequencies, it has been determined that bacteria and fungi prevent their life and reduce their activity, while lower frequency acoustic signals have no effect on larger organisms effective against fish (Council, 1996). This method was not used because of its high cost and low efficiency.

Inhibition of fouling organisms has been tried to be prevented by the use of various homo and copolymers. These are zwitterionic polymers (G. Li et al., 2008; Zhao, Ye, Hu, Wang, & Zhou, 2014), biodegradable hydrophilic or amphiphilic polymers (Carteau et al., 2014; Ma et al., 2014), bio-based topographies (Brzozowska et al., 2014; Wei et al., 2014), organic inorganic nanostructured hybrid systems (J. Li & Wang, 2014; Yee et al., 2014), low surface energy elastomers (Bacha, Méghabar, & Technology, 2014), It has been used for the preparation of antifouling coatings (Q. Sun et al., 2015). The Shark surface effect has been invaluable for the fabrication of biomimetic antibiological pollution coatings (Chen et al., 2014).

4. Results

The increase in maritime transport over time has led to an increase in the maritime trade fleet. In the last 30 years, the world maritime trade fleet has grown 3 times. In addition to this, oil and natural gas exploration in the sea has increased in recent years. As a result, the demand for antifouling coating used in drilling rigs has increased. While the antifouling market in 2007 was around US $ 4 billion annually (Dafforn et al., 2011), it is expected to reach a value of around US $ 23 billion by the end of 2023 (antifouling-coatings-market).

The sector has grown almost 6 times in the last 15 years. China, South Korea, and Japan are the countries that build the most ships in the world, respectively. These three countries are responsible for more than 90 % of the world's shipbuilding industry (UNCTAD, 2019). Parallel to this, the region that maintains its dominance in the antifouling market is the Asia Pacific. This region is followed by North America, Europe, and Latin America, respectively (antifouling-coatings-market).

The demand for antifouling coatings against unwanted fouling organisms adhering to underwater parts of ships and marine platforms is rapidly increasing. In this context, intensive research and development studies on the subject are carried out in both industry and academic institutions worldwide. There is a great need for antifouling materials that are low in cost, high efficiency, do not contain heavy metals, and do not harm the environment.

Even from moderate to low reduction of fouling organisms, costs have highly decreased (M. Schultz et al., 2011). The costs of scientific and technological research and development activities to develop organic adhesion-reducing (antifouling) materials are much less than the damage caused by fouling organisms to the maritime industry. Moreover, the economic, social, and environmental gains of research conducted on this subject are extremely high. In this context, it is important that R&D studies for the development of environmentally friendly organic anti-adherence coatings and coatings are supported by the maritime sector. Especially, encouraging and developing university-industry cooperation in this field will significantly reduce the fuel costs and emissions of ships.

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Chapter 4

EVALUATION OF RENEWABLE ENERGY OPTIONS BASED ON INTEGRATED BEST–WORST AND ADDITIVE RATIO ASSESSMENT

Mehmet ŞAHİN[1]

1 Department of Industrial Engineering, Iskenderun Technical University, 31200 Iskenderun, Turkey, mehmet.sahin@simon.rochester.edu, ORCID: https://orcid.org/0000-0001-7078-7396

1. Introduction

Each incident shows how dependent people are on energy and how vitally important it is for people. The most current and concrete proof of this is COVID-19, which takes the whole world under its influence. Also, the global energy demand is continuously growing due to economic and population growth and technological improvements, especially in developing countries (OECD, 2012). Traditional energy sources have catastrophic impacts on human health and the environment because of greenhouse emissions (Sovacool, 2012). With the deterioration of the global climate and a growing shortage of fossil fuels, more attention has been given to renewable energy (Ellabban, Abu-Rub, & Blaabjerg, 2014). Renewable energy sources are a valuable and sustainable source of clean energy in environmental health by decreasing greenhouse gas emissions. Also, renewable energy technologies are the most growing energy sources in the world.

As a developing country, Turkey has prioritized the transition to renewable energy sources. Developing countries such as Turkey need to give great importance to sustainable and renewable energy sources to be successful on the road to development. The fact that fossil fuels have been the primary source of electricity generation in Turkey raises several concerns, including carbon emission, public health, cost, depletion of fossil fuels, and environmental damages (Day & Day, 2017; Höök & Tang, 2013; Perera, Ashrafi, Kinney, & Mills, 2019). The ratios of electricity generation options in Turkey are 31.2% for hydroelectric, 8.3% for wind, 6.6% for solar PV, 1.3% for biomass, and 1.7% for geothermal in terms of installed capacity as of December 2019 (TEIAS, 2020). The share of renewable energy technologies has been continuously increasing and has exceeded 49% in 2019. Each of these technologies has its own advantages and disadvantages. Also, considering factors such as the required time for installation and installation and maintenance costs, the selection of the optimal ones becomes even more critical.

The ever-increasing demand and scarcity of resources necessitate the correct and effective use of energy resources. Choosing the optimal renewable energy technology is a vital decision for countries, and indeed for the world. The determination of the best energy option and the availability of many contradictory criteria indicate that the selection of renewable energy options is a typical multicriteria decision-making (MCDM) problem. MCDM methods have been efficaciously implemented for such problems. Analytic network process (ANP) (Alizadeh, Soltanisehat, Lund, & Zamanisabzi, 2020), weighted sum method (WSM), technique for order of preference by similarity to ideal solution (TOPSIS), elimination et choice translating reality (ELECTRE) (Campos-Guzmán, García-Cáscales, Espinosa, & Urbina, 2019; Lee & Chang, 2018), analytic hierarchy process (AHP) (Wu, Xu, & Zhang, 2018), vlsekriterijumska optimizacija i kompromisno resenje (VIKOR) (Rani et al., 2019), stepwise weight assessment ratio analysis (SWARA) (Zolfani & Saparauskas, 2013), and additive ratio assessment (ARAS) (Ghenai, Albawab, & Bettayeb, 2020) were used. In addition, Wang, Xu, and Solangi (2020) implemented fuzzy AHP to assess the renewable energy resources of Pakistan and posited that wind energy was the optimal alternative. Ali, Chiu, Aghaloo, Nahian, and Ma (2020) presented a hybrid approach based on the best-worst method (BWM), integrated determination of objective criteria weights, and evaluation based on distance from average solution for ranking the power generation technologies in Bangladesh and claimed that gas power generation technology was the best, and wind was the worst. Zhang, Xin, Yong, and Kan (2019) evaluated the renewable energy project performance in China based on a hybrid MCDM approach based on TODIM (an acronym in Portuguese for interactive multicriteria decision-making) and claimed that the best alternative was the wind power project.

BWM has been applied to numerous problems in various fields. van de Kaa, Fens, and Rezaei (2019) and Bonyani and Alimohammadlou (2018) used BWM to assign relative importance to criteria in energy. Omrani, Alizadeh, and Emrouznejad (2018) utilized fuzzy BWM for determining the optimal combination of power plant alternatives. Rezaei, Papakonstantinou, Tavasszy, Pesch, and Kana (2019) utilized BWM for finding attribute weights in the evaluation of a sustainable product-package design problem. ARAS has also been implemented for different problems in various fields. It was used for evaluation and ranking, research and technology organizations (Varmazyar, Dehghanbaghi, & Afkhami, 2016), building sustainability (Medineckiene, Zavadskas, Björk, & Turskis, 2015), electro-discharge machine process parameters (Kumar, Hussain, & Rai, 2019), and catering supplier (Fu, 2019).

The literature review reveals that BWM and ARAS were successfully used for decision problems in different areas. However, they have not been used for ranking renewable energy options as integrated. The present study's primary objective is to assess renewable energy technologies in Turkey using the integrated BWM and ARAS methods for the first time. In this context, BWM is used for finding weights of the criteria, namely levelized cost of electricity, maximum incentive, job creation, accident-related fatality, land use, water use, greenhouse gas emission, electricity mix share, and efficiency. The output of BWM is used as input for ARAS. Also, the required data are collected from reliable sources, including official institutions. Then, the renewable energy technologies in Turkey are evaluated through the results of ARAS.

The remainder of the study is organized as follows. The methods used and the approach proposed are described in the following section. Section 3 presents the results and discussion. Section 4 describes the conclusions and possible future research directions.

2. Materials and Methods

The description of the BWM and ARAS methods is presented first. Then, the proposed methodology is presented in the following subsections.

2.1. Best–Worst Method (BWM)

Rezaei (2015) presented BWM, which is based on the comparisons of criteria and is used to obtain the criteria weights. It is a subjective approach, the result of which is shaped according to the decision-maker's assessment as AHP. Subjectivity can be interpreted as a disadvantage of this approach because the result can be misleading due to the lack of expertise. However, this approach's prominent advantages include fewer time requirements for comparisons, easy comparisons through integers, and consistent results compared with the AHP. The procedure of the BWM can be described as follows (Rezaei, 2015):

1. A decision criterion set is designed. The decision-maker determines the *n* criteria $\{c_1, c_2, \ldots, c_n\}$.
2. The best and worst attributes overall are identified.
3. The preference of the best attribute over all other attributes is identified via the scale from 1 to 9. The best-to-others vector is established as follows:

   $$A_B = (a_{B1}, a_{B2}, \ldots, a_{Bn})$$

   where a_{Bj} denotes the preference of the best attribute B over criterion j and $a_{BB} = 1$.
4. Pairwise comparisons between the worst attribute and other attributes are designed. The others-to-worst vector is established as follows:

   $$A_W = (a_{1W}, a_{2W}, \ldots, a_{nW})^T$$

   where a_{jW} denotes the preference of attribute j over the worst attribute W and $a_{WW} = 1$.

5. The optimal weights $(w_1^*, w_2^*, \dots, w_n^*)$ are computed, such that the maximum absolute differences $\left|\frac{w_B}{w_j} - a_{Bj}\right|$ and $\left|\frac{w_j}{w_W} - a_{jW}\right|$ are minimized for all j. The min–max model is established accordingly as follows:

$$\min \max_j \left\{ \left|\frac{w_B}{w_j} - a_{Bj}\right|, \left|\frac{w_j}{w_W} - a_{jW}\right| \right\}$$

subject to

$$\sum_j w_j = 1$$

$$w_j \geq 0, \text{for all } j$$

The previous model can be converted to the following model:

$$\min \xi$$

subject to

$$\left|\frac{w_B}{w_j} - a_{Bj}\right| \leq \xi, \text{for all } j$$

$$\left|\frac{w_j}{w_W} - a_{jW}\right| \leq \xi, \text{for all } j$$

$$\sum_j w_j = 1$$

$$w_j \geq 0, \text{for all } j$$

The optimal weights $(w_1^*, w_2^*, \dots, w_n^*)$ and ξ^* are determined after solving this model.

6. The consistency of the comparison matrix is controlled to assure overall consistency. The consistency ratio is calculated using the following function (*CR*: consistency ratio; *CI*: consistency index):

$$CR = \frac{\xi^*}{CI} \quad (2.1)$$

Table 1 presents the consistency index values. High consistency index values indicate that the comparisons are reliable.

Table 1. Consistency index (CI) values

a_{BW}	1	2	3	4	5	6	7	8	9
CI	0	0.44	1	1.63	2.3	3	3.73	4.47	5.23

2.2. Additive Ratio Assessment (ARAS)

ARAS was presented by Zavadskas and Turskis (2010). The implementation of the ARAS method requires the following steps:

1. Normalizing the decision matrix. The benefit and cost attributes are normalized based on the following functions, respectively.

$$r_{ij}^{*} = \frac{r_{ij}}{\sum_{i=0}^{m} r_{ij}} \; for\, j = 1,2,\dots,n$$
$$r_{ij} = \frac{1}{r_{ij}^{**}};\; r_{ij}^{*} = \frac{r_{ij}}{\sum_{i=0}^{m} r_{ij}} \; for\, j = 1,2,\dots,n \qquad (2.2)$$

2. Obtaining the attribute weights (w_1, w_2, …, w_n) from BWM, and calculating the weighted normalized decision matrix via the following function:

$$\widehat{r_{ij}} = r_{ij}^{*} * w_j \; for\, i = 0,1,\dots,m;\; j = 1,\dots,n \qquad (2.3)$$

3. Obtaining the optimality function (S_i) through the following equation. The higher value of the optimality function indicates the better.

$$S_i = \sum_{j=1}^{n} \widehat{r_{ij}} \; for\, i = 0,1,2,\dots,m \qquad (2.4)$$

4. Obtaining the utility degree and ranking alternatives accordingly. The utility degree (K_i) for the *i*th alternative is obtained based on the following equation. The option with the highest utility degree is the best.

$$K_i = \frac{S_i}{S_0} \; for\, i = 0,1,2,\dots,m \qquad (2.5)$$

where S_0 is the optimality value of S_i.

2.3. The Proposed Approach

The main steps of the proposed alternative ranking approach in renewable energy based on BWM and ARAS are presented in Figure 1.

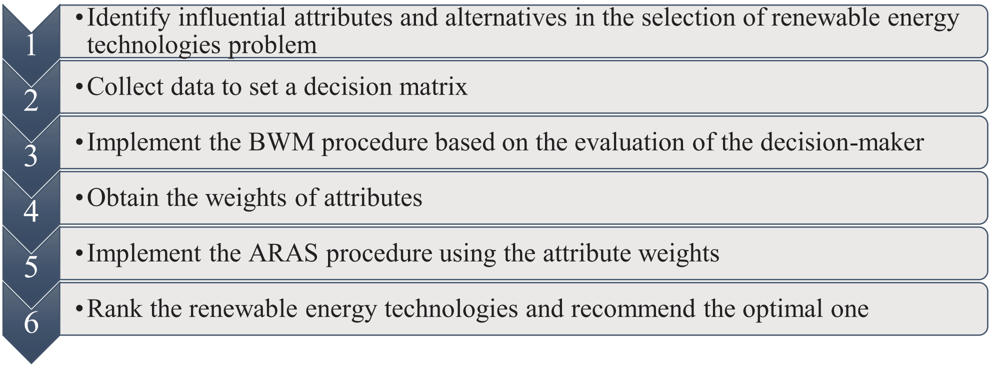

Figure 1. The steps of the proposed approach

First, the determination of the most influential criteria and renewable energy technologies is made based on a comprehensive literature review and expert knowledge. In this context, economic (levelized cost of electricity (LCOE) and maximum incentive), socioeconomic (job creation and accident-related fatality), environmental (land use, water use, and greenhouse gas (GHG) emission), and technical (electricity mix share and efficiency) criteria are determined. Table 2 presents the selected criteria and the unit of each. Hydropower, wind (onshore), geothermal, biomass, and solar photovoltaic (PV) renewable energy technologies are the alternatives. Second, data is collected for each criterion and alternative from different sources (Evans, Strezov, & Evans, 2017; Industrial Development Bank of Turkey, 2019; IRENA, 2019; TEIAS, 2020; Turkish Energy Foundation, 2017) to establish the decision matrix.

Third, the BWM method is implemented to obtain criteria weights required as input for the ARAS method. As explained previously, in BWM, the most important (best) and the least important (worst) criteria are initially found, as given in Table 3. Then, the best-to-others vector is determined, as presented in Table 4.

Table 2. Selected criteria and their units

Criteria	Unit
LCOE (C1)	USD/kWh
Maximum incentive (C2)	US Cent/kWh
Land use (C3)	m^2/kWh
Water use (C4)	kg water/kWh
GHG emission (C5)	g CO_2-e/kWh
Job creation (C6)	avg. job years/GWh
Accident-related fatality (C7)	Fatalities/GWe-yr
Electricity mix share (C8)	%
Efficiency (C9)	%

Table 3. Identified best and worst criteria

Best (most important)	C1
Worst (least important)	C7

Table 4. Preference of the best attribute compared with the other attributes

Best-to-others	C1	C2	C3	C4	C5	C6	C7	C8	C9
C1	1	2	4	4	3	3	5	4	2

Then, the worst-to-others vector is set, as presented in Table 5.

Table 5. Preference of all attributes compared with the worst attribute

Others to the Worst	C7
C1	5
C2	4
C3	2
C4	2
C5	2
C6	2
C7	1
C8	3
C9	4

Fourth, after solving the model, the weights of the criteria are obtained. These weights are used as an input for the ARAS method. In the fifth phase of the proposed approach, the decision matrix is initially normalized, as presented in Table 6. To be noted that, the first row in the table indicates the optimal values. Then, the weighted normalized values are determined, as presented in Table 7.

Table 6. Normalized decision matrix

C1	C2	C3	C4	C5	C6	C7	C8	C9
0.208	0.216	0.471	0.476	0.248	0.330	0.421	0.401	0.331
0.208	0.104	0.035	0.000	0.248	0.102	0.038	0.401	0.331
0.175	0.119	0.009	0.476	0.248	0.064	0.055	0.099	0.125
0.136	0.142	0.003	0.000	0.038	0.095	0.059	0.018	0.055
0.115	0.216	0.471	0.048	0.076	0.330	0.421	0.072	0.048
0.158	0.204	0.011	0.000	0.143	0.080	0.007	0.009	0.109

Table 7. Weighted normalized values

C1	C2	C3	C4	C5	C6	C7	C8	C9
0.052	0.032	0.035	0.035	0.024	0.032	0.017	0.030	0.049
0.052	0.015	0.003	0.000	0.024	0.010	0.002	0.030	0.049
0.043	0.017	0.001	0.035	0.024	0.006	0.002	0.007	0.018
0.034	0.021	0.000	0.000	0.004	0.009	0.002	0.001	0.008
0.029	0.032	0.035	0.004	0.007	0.032	0.017	0.005	0.007
0.039	0.030	0.001	0.000	0.014	0.008	0.000	0.001	0.016

Then, the optimality function values are calculated, as presented in Table 8. These values are used to find the utility degrees of each alternative. Finally, the rank of alternatives is determined based on these values. After ranking these values, the option with the highest utility value is recommended as the optimal alternative.

Table 8. Optimality function values

0	0.305
1	0.184
2	0.155
3	0.080
4	0.168
5	0.109

3. Results and Discussion

The attribute weights obtained through BWM are presented in Table 9. LCOE has the highest weight, followed by maximum incentive, efficiency, GHG emission, job creation, land use, water use, electricity mix share, and accident-related fatality.

Table 9. Weights of attributes

Attribute	Weight
LCOE	0.248
Maximum incentive	0.147
Land use	0.074
Water use	0.074
GHG emission	0.098
Job creation	0.098
Accident-related fatality	0.040
Electricity mix share	0.074
Efficiency	0.147

To demonstrate the significance level of each attribute and to allow comparisons of attributes, Figure 2 is presented. The figure demonstrates the importance level difference between LCOE and accident-related fatality attributes.

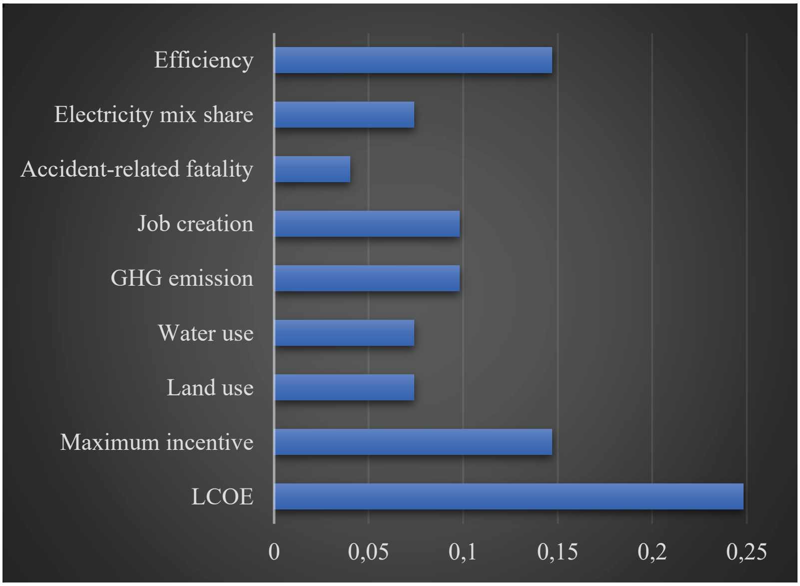

Figure 2. Comparison of attribute weights

Based on these attribute weights, the utility values and ranking of the renewable energy technologies are determined through ARAS, as presented in Table 10.

Table 10. Utility values and the final ranking of renewable energy technologies

Options	Utility degree	Final ranking
Hydroelectric	0.602	1
Wind (onshore)	0.509	3
Geothermal	0.261	5
Solar PV	0.549	2
Biomass	0.357	4

The results designate that the optimal renewable energy technology is hydro, followed by solar PV, onshore wind, biomass, and geothermal. Hydroelectric power plants generate electricity using the potential energy difference between the two points where water is located. Hydroelectric is the leading renewable energy technology in the world as it provides about one-fifth of the electricity need of the world.

Thus, the outcome of this study is consistent with the situation in real life. Solar PV technology is a substantial energy source in sunny countries, such as Turkey. Despite its biggest drawback not being productive at night, Solar PV is a competitive and effective alternative. It was ranked second in this study. Furthermore, being one of the most environmentally friendly renewable energy technologies, the share of wind option has been increasing in the world. The concerns about the impact of biomass on the environment can impede its wide use. Unlike solar and wind options, geothermal energy can provide continuous electricity.

To sum up, each renewable energy technology has its advantages and drawbacks. Based on the attributes considered in this study and considering Turkey's case, hydro is the optimal energy option for Turkey. To compare this result with those of previous studies, several studies were considered. Kabak and Dağdeviren (2014) evaluated the renewable energy sources in Turkey using a hybrid model and claimed that hydro was the optimal alternative. Shen, Chou, and Lin (2011) examined the renewable energy sources in Taiwan and determined that hydro was the optimal alternative. Şengül, Eren, Eslamian Shiraz, Gezder, and Şengül (2015) also found hydro as the optimal renewable energy source for Turkey. In some other studies, hydroelectric was also found as the best option for Turkey (Atilgan & Azapagic, 2016; Özkale, Celik, Turkmen, & Cakmaz, 2017). The number of studies whose results are consistent with this study can be expanded. Admittedly, numerous studies recommend other renewable energy sources as optimal. It is hard to say that this is the best solution or recommendation. The fact that the outcome of the MCDM method is dependent on the weighting method, choosing any of them causes the outcome to be different. Also, each MCDM method has its procedure that generates different rankings. Analyzing a problem using different MCDM methods may contribute to finding the optimal solution. This study is important in this regard. The assessment of renewable energy sources of Turkey is made based on the integrated BWM and ARAS method for the first time. Thus, an evaluation from a different perspective was presented.

4. Conclusion

This study presented an integrated method of BWM and ARAS for evaluating renewable energy technologies in Turkey. It is the first time to utilize both methods to rank renewable energy options. In this regard, five options were evaluated based on economic (LCOE and maximum incentive), socioeconomic (job creation and accident-related fatality), environmental (land use, water use, and GHG emission), and technical (electricity mix share and efficiency) attributes. The BWM results designated that the LCOE was the most important attribute, whereas accident-related fatality was the least important. The ARAS results indicated that hydro is the optimal renewable energy technology in Turkey, followed by solar PV, onshore wind, biomass, and geothermal.

This study has some limitations. First, the number of attributes might be increased for more detailed analysis. Second, the most updated data could reveal the latest ranking of energy technologies. However, it is not possible to obtain such data at the moment. Last, subjective evaluations might change over time; therefore, the use of other weighting methods might improve the analysis.

Future studies may include additional attributes, weighting methods, and MCDM methods to extend the analysis. Considering the weights affecting the result of the MCDM method, the use of different kinds of objective and subjective methods may improve the quality of future studies.

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Chapter 5

TRIANGULAR BOWTIE ANTENNA DESIGN AND MODELLING

Ahmet Arif ULUSLU[1]

1 Öğr. Gör. Dr., İstanbul Üniversitesi-Cerrahpaşa
ORCID ID: 0000-0002-5580-1687

1- INTRODUCTION

Microwave antenna stages continue to be one of the most important elements for wireless communication systems. The geometric variables of antenna designs are the most important design parameters that determine the operating frequency, return loss characteristics and directionality of the antenna designs. However, similar to any microwave circuit design, microwave antenna designs have complex (linear and nonlinear) relationships between geometric design variables and performance measures; where variation in any geometric design parameter has a devastating effect on the improvement of one of the performance metrics. other performance measures. Therefore, determining the optimal geometric design parameters of a microwave antenna design can be considered as a multi-dimensional, multi-purpose optimization problem. Here, microwave antenna design is thought to create the optimal characterization of Multiobjective Optimization antenna designs, a new fast and powerful optimization algorithm to achieve the challenging design optimization problem. In addition, the Moment Method (MOM) has been used to accurately calculate gain and return loss performance measurements of the antenna design according to changes in geometric design parameters. Then the performance measure obtained was to create a cost function to be used in the design optimization problem. The antenna parameters, which have the lowest cost function, were selected among the found solutions and the design process was made.

2- OPTIMAL SOLUTIONS

If there is no other solution that dominates a solution found, this solution is called the optimal solution. In other words, a goal cannot be resolved without negatively affecting at least one other target. The corresponding target vector F(a) is called a dominant vector or a non-sub or non-dominant vector. A solution is said to be optimal, but if and only if there is no other solution dominating it, in other words, a goal cannot be solved without negatively affecting at least one other goal. The set of all optimal solutions is called the optimal solution set. The corresponding objective vectors are said to be at their optimal limit. It is often impossible to find an analytical expression of its optimal limit. Figure 1 gives the flow diagram to be followed to obtain the optimal characteristics of a Microwave antenna.

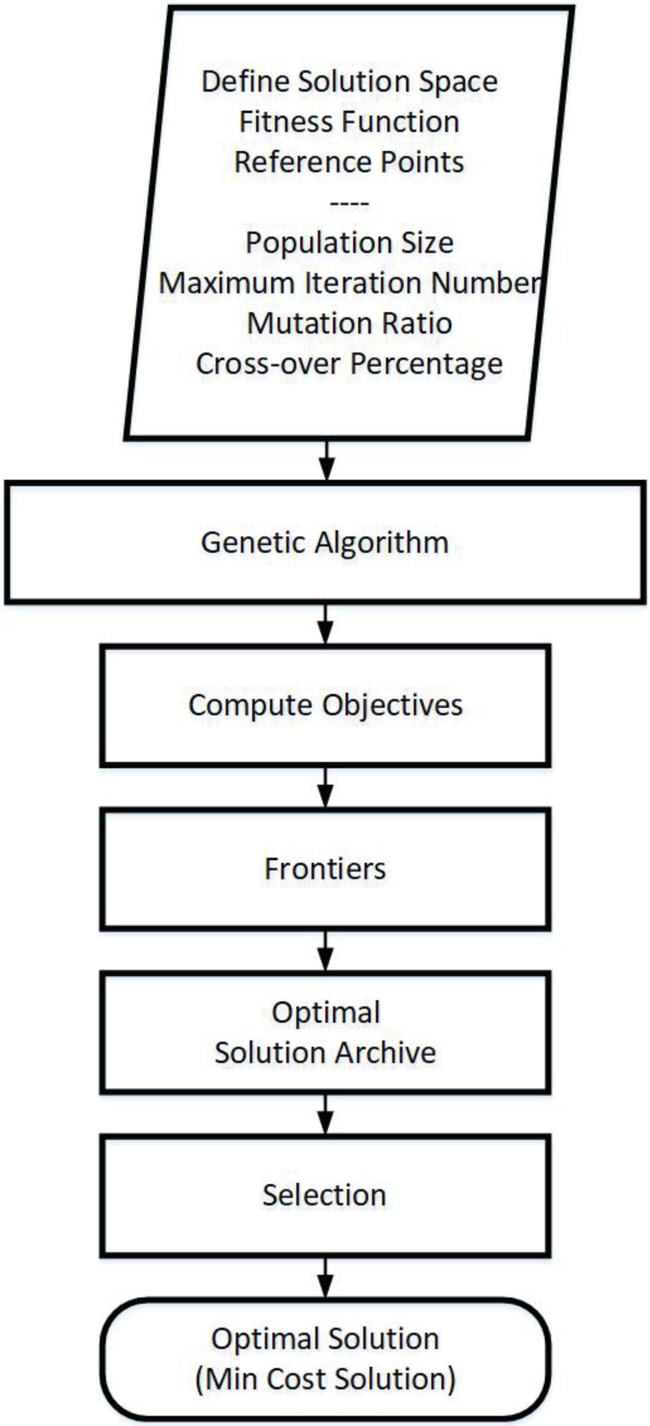


FIGURE 1 *Flow Chart*

3- ARTIFICIAL NEURAL NETWORKS

Artificial neural networks, or to put it briefly, ANN; It emerged as a result of efforts to artificially simulate the working system of the human brain. In the most general sense, an ANN can be considered as a complex system that exists as a result of connecting many neurons (nerve cells) in the human brain, or artificially simple processors to each other with different levels of influence. The studies, which started with the mathematical modelling efforts of neurons in the human brain in basic medical units, have taken a disciplined form in the past fifteen years. Today, ANN has been used in research in many different disciplines such as physics, mathematics, electrical engineering and microwave electronics. Practical use of artificial neural networks is generally to quickly identify and detect information data, which can be found in many different structures and forms. In fact, the most important reason for the wide use of artificial neural networks in engineering applications is that it creates an effective and fast alternative for difficult problems with classical techniques. Because although computers are hundreds of times successful in terms of speed and accuracy in mathematical and algorithmic calculations such as multiplication and division, where the human brain ability is weakest, they still cannot perform functions of the human brain such as learning and recognition fast enough.

4- ANTENNA DESIGNS TRIANGULAR BOWTIE ANTENNA

The Bowtie antenna is a planar shape of bionic dipole antennas. Bowtie antennas have many advantages such as light weight, low cost, low profile, symmetrical radiation pattern, making them available for wireless communication systems, ground penetrating radar (GPR) etc. It makes it one of the widely used antenna models for applications [1-5]. However, performance measures of the design are largely dependent on geometric design values. Therefore, the design of bowtie antennas can be considered as a multi-purpose multi-dimensional design optimization problem. In this study, a working case of the application of the genetic algorithm for the multi objective optimization of antenna design, a triangular microstrip bowtie antenna is considered. The power feeding part of the bowtie antennae is made from the point between two triangular plates. With these features, bowtie antennas can be considered as dipole antenna type in a way. Schematic and design parameters of the antenna design are given in Figure 2.

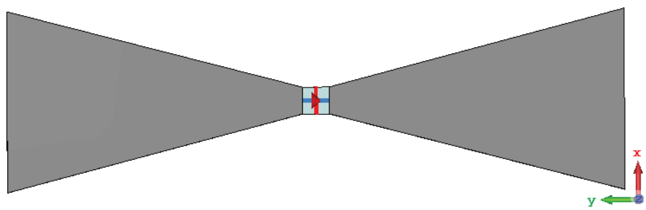


FIGURE 2 *Bow Tie Antenna*

4.1 Optimal Algorithm Parameter Set Selection for Bowtie Triangular Antenna

The default parameters for the algorithm are accepted as Population = 50, Maximum iteration = 50, Mutation = 0.5 and Cross-over Percentage = 0.5. Here we experimented with different parameters to use the most optimal parameters and Population = 50; Maximum iteration = 80; mutation = 0.8, Cross-over Percentage = 0.3. For the results found in this application, it is selected as the optimum parameter set for all operations of the algorithm originating from 2.4 GHz. Figures 3A, B, C show typical Cost and Function Evaluation Number (FEN) variations with Repeat of Best Performance selected from 10 different runs for Cross-over Percentage (Pc) = 0.5, Mutation (Pm) = 0.5, and Maximum Iteration = 10, 15, 20, the trio (Directivitymax S_{11}min) in Population (N) taken as parameter (2.4GHz). Figure 4 shows typical Cost and Function Assessment Number (FEN) variations with Repeat of Best Performance selected from Top iterations = 20, Population (N) = 50, ($Directivity_{max}$ S_{11min}) triple, (2.4 GHz) Crosswise 10 runs - Cross-over Percentage (P_C) and Mutation (P_m) taken as parameters, respectively. Also, the Cost and Science variations numerical tables in tables 1 and 2, respectively.

TABLE 1 *Performance Evaluations with respect to maximum Iteration and Population throughout for the Bowtie Triangular Antenna, at (2.4GHz).*

Max Iteration	Population		Maximum	Minimum	Mean
10	30	Cost	1.67	0.97	1.45
		FEN	330	330	330
10	50	Cost	1.69	0.94	1.50
		FEN	550	550	550
10	80	Cost	1.69	0.95	1.53
		FEN	880	880	880
10	100	Cost	1.69	0.92	1.51
		FEN	1100	1100	1100
15	30	Cost	1.68	0.93	1.55
		FEN	481	481	481
15	50	Cost	1.67	0.95	1.46
		FEN	800	800	800
15	80	Cost	1.67	0.92	1.51
		FEN	1280	1280	1280
15	100	Cost	1.67	0.92	1.50
		FEN	1601	1601	1601
20	30	Cost	1.68	0.92	1.40
		FEN	632	632	632
20	50	Cost	1.59	0.92	1.33
		FEN	1050	1050	1050
20	80	Cost	1.66	0.94	1.38
		FEN	1681	1681	1681
20	100	Cost	1.58	0.92	1.34
		FEN	2100	2100	2100

TABLE 2 *Performance Evaluations for 10 runs of Cost with respect to Crossover and Mutation Percentage throughout for the Bowtie Triangular Antenna, at (2.4GHz).*

Crossover Percentage	Mutation Percentage		Maximum	Minimum	Mean
0.3	0.3	Cost	1.69	0.96	1.49
		FEN	1052	1052	1052
0.3	0.5	Cost	1.65	0.97	1.40
		FEN	1051	1051	1051
0.3	0.8	Cost	1.59	0.90	1.36
		FEN	1051	1051	1051
0.5	0.3	Cost	1.65	0.93	1.43
		FEN	1050	1050	1050
0.5	0.5	Cost	1.59	0.92	1.33
		FEN	1050	1050	1050
0.5	0.8	Cost	1.60	0.93	1.32
		FEN	1051	1051	1051
0.8	0.3	Cost	1.70	0.94	1.37
		FEN	1051	1051	1051
0.8	0.5	Cost	1.69	0.91	1.41
		FEN	1050	1050	1050
0.8	0.8	Cost	1.60	0.94	1.42
		FEN	1051	1051	1051

4.2 Weighting Coefficient

Parameters selected in the previous section Typical Cost and Function Evaluation Number (FEN) for 10 runs, Max Iteration=20, Population (N)=50, Cross-over Percentage (P_C)=0.3 and Mutation (P_m)=0.8. Figures 5A,B,C denote typical Cost and Function Evaluation Number (FEN) variations with Iteration of the Best Performance chosen among 10 runs for Max Iteration=20, Population (N)=50, Cross-over Percentage (P_C)=0.3 and Mutation (P_m)=0.8, the ($Directivity_{max}$ S_{11min}) triple, at (2.4GHz) as weighting coefficient-1 (w_1) and weighting coefficient-2 (w_2) taken as parameters, respectively. Besides, Cost and Fen variations in numerical tables in tables 3, respectively.

TABLE 3 *Performance Evaluations for 10 runs of Cost with respect to weighting coefficient-1(w1) and weighting coefficient-2(w2) throughout for the Bowtie Triangular Antenna, at (2.4GHz) using the selected parameters Max iteration=20, Population=50, Cross-over Percentage=0.3, Mutation=0.8*

w_1	w_2		Maximum	Minimum	Mean
10	10	Cost	1.53	0.83	1.21
		FEN	1052	1052	1052
10	20	Cost	1.59	0.90	1.36
		FEN	1051	1051	1051
10	30	Cost	1.61	1.07	1.43
		FEN	1050	1050	1050
10	40	Cost	1.67	1.16	1.52
		FEN	1052	1052	1052
10	50	Cost	1.69	1.28	1.56
		FEN	1050	1050	1050
20	10	Cost	1.67	0.92	1.33
		FEN	1050	1050	1050
20	20	Cost	1.74	1.05	1.49
		FEN	1052	1052	1052
20	30	Cost	1.77	1.17	1.55
		FEN	1051	1051	1051
20	40	Cost	1.76	1.12	1.67
		FEN	1052	1052	1052
30	10	Cost	1.80	0.95	1.31
		FEN	1053	1053	1053
30	20	Cost	1.80	1.04	1.52
		FEN	1051	1051	1051
30	30	Cost	1.83	1.23	1.63
		FEN	1051	1051	1051
30	40	Cost	1.82	1.23	1.71
		FEN	1051	1051	1051

4.3 Obtaining the Data Set

Optimal Limits of Bowtie Triangle Antenna are achieved for 2 performance trio of 1 sample frequency given at 2.4GHz ($Directivity_{max}$ S_{11min}) Typical Boundaries of Bowtie Triangle Antenna in Figures 6A, B, C, D, E, Figures 7A, B, C, D and Figures 8A, B, C, D which belong to the triplets Directivity (dB) - S_{11} (respectively $Directivity_{max}$ S_{11min}) DB) plane at 2.4GHz. Therefore, as a design feature, a minimum S_{11} with maximum Directivity, which is the point closest to the vertical axis, can be selected.

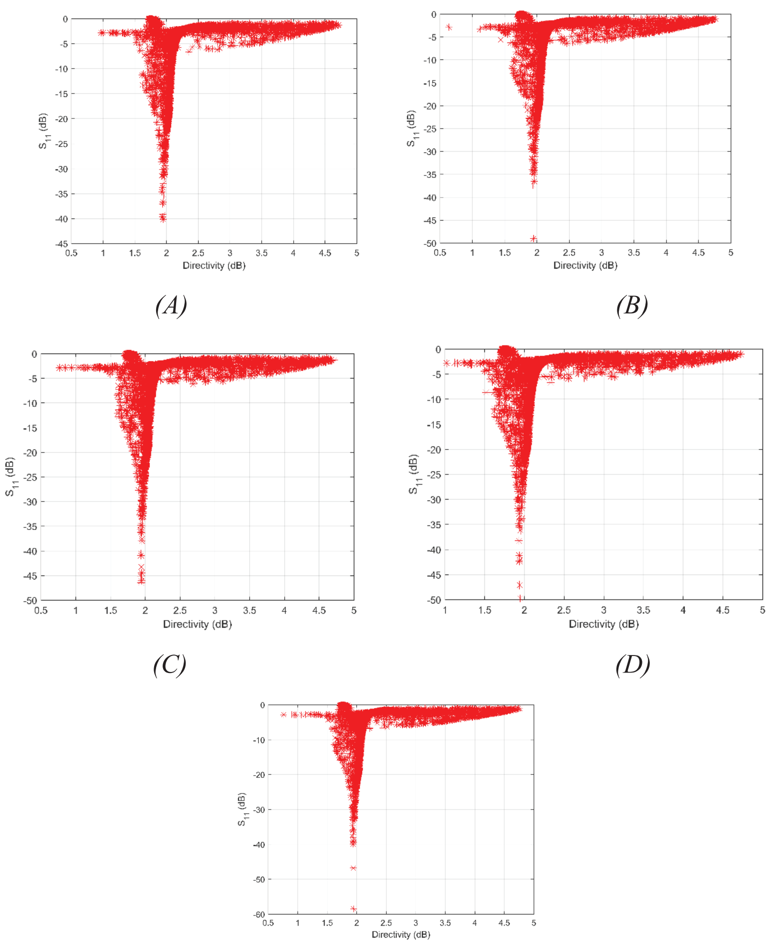
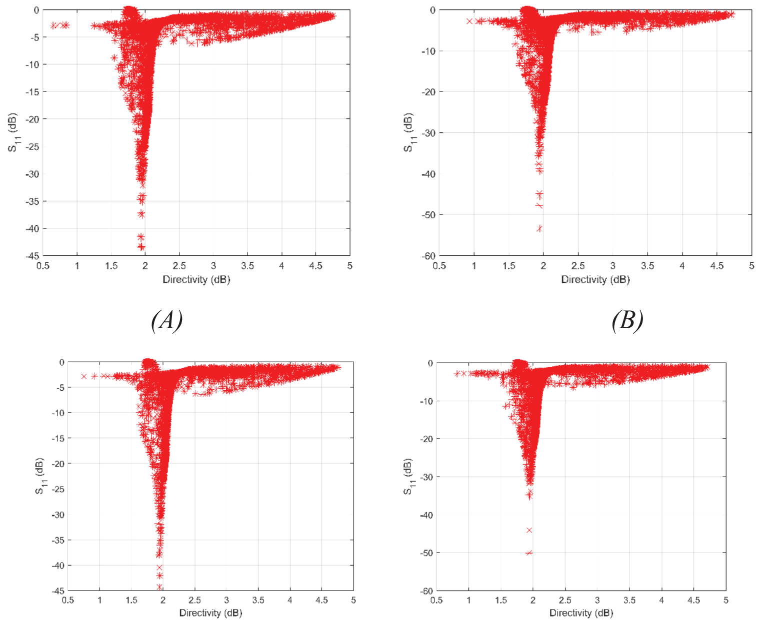


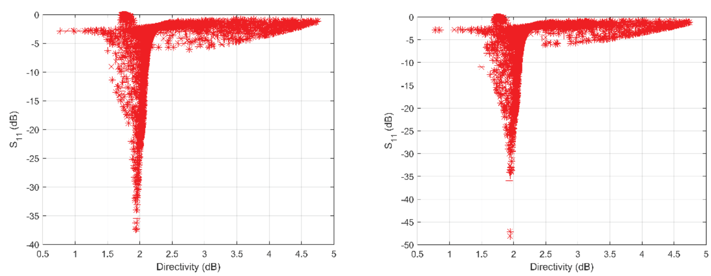
FIGURE 6 *Optimal Frontiers for the Bowtie Triangular Antenna, at (2.4GHz), weighting coefficient-1 (w1)=10: (A) weighting coefficient-2 (w2)=10, (B) weighting coefficient-2 (w2)=20, (C) weighting coefficient-2 (w2)=30, (D) weighting coefficient-2 (w2)=40, (E) weighting coefficient-2 (w2)=50*



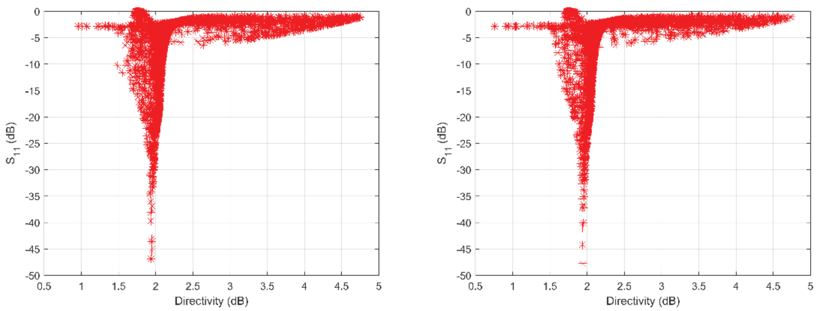
(A) (B)

(C) (D)

FIGURE 7 *Optimal Frontiers for the Bowtie Triangular Antenna, at (2.4GHz), weighting coefficient-1 (w1)=20: (A) weighting coefficient-2 (w2)=10, (B) weighting coefficient-2 (w2)=20, (C) weighting coefficient-2 (w2)=30, (D) weighting coefficient-2 (w2)=40*



(A) (B)



(C) (D)

FIGURE 8 *Optimal Frontiers for the Bowtie Triangular Antenna, at (2.4GHz), weighting coefficient-1 (w1)=30: (A) weighting coefficient-2 (w2)=10, (B) weighting coefficient-2 (w2)=20, (C) weighting coefficient-2 (w2)=30, (D) weighting coefficient-2 (w2)=40*

4.4 Optimal Solution Modelling

In this part, 65 test data were studied. Some of the data were used as training and some as a test. Modeling was done using ANN model. 25% of all data were used as training data. The results obtained are shown in Table 4. The proposed ANN model is shown in Figure 9. The input layer in Figure 9 represents the input parameters in Table 4. The number of neurons in the hidden layer is adjusted by the algorithm. The parameters in the output layer show the modeled output values in Table 4. Initial connection weights and bias values are chosen randomly. During the study, the optimum value was tried to be obtained as a result of many trials.

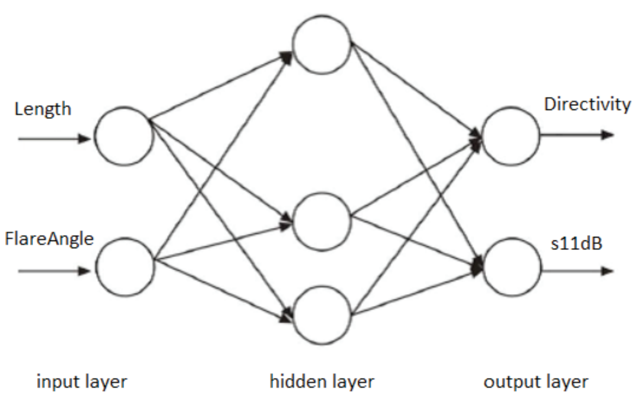


FIGURE 9 *Artificial Neural Network Model Developed*

TABLE 4 *Comparison of the proposed ANN model and the values found as a result of the Optimization*

Inputs Values		**Optimal Output Values**		**Modeled Output Values**	
Length	FlareAngle	Directivity	S_{11} (dB)	Directivity	S_{11} (dB)
0.04432948	27.38038531	1.9457	-40.1613	1.9448	-45.1216
0.04397579	28.97654274	1.9379	-39.6150	1.9401	-43.8399
0.04415374	28.96268141	1.9417	-39.1386	1.9402	-43.8744
0.04326851	31.20753409	1.9360	-37.0346	1.9354	-38.4940
0.04431923	27.24180441	1.9435	-36.6911	1.9453	-44.6664
0.04440232	27.28776428	1.9460	-49.0252	1.9451	-44.8285
0.04389339	29.23851875	1.9367	-37.3019	1.9392	-43.1472
0.04481467	24.95986791	1.9561	-36.5201	1.9543	-36.3606
0.04463626	25.18290581	1.9531	-34.9627	1.9529	-37.1092
0.04460682	25.39809095	1.9508	-34.9681	1.9516	-37.8727
0.04429163	28.12534771	1.9421	-46.4562	1.9425	-45.6189
0.04442001	27.19872103	1.9446	-46.0764	1.9455	-44.5055
0.04409152	28.68422887	1.9395	-45.2425	1.9410	-44.5434
0.04458661	26.53479367	1.9488	-44.4827	1.9477	-41.6937
0.04407235	29.09741291	1.9406	-43.2484	1.9397	-43.5312
0.04448479	26.99492211	1.9478	-49.7860	1.9462	-43.6598
0.04416031	28.55136452	1.9402	-47.0943	1.9414	-44.8455
0.04387315	30.22394207	1.9363	-42.3623	1.9360	-40.1095
0.04403426	28.82606423	1.9406	-42.1290	1.9406	-44.2079
0.04394332	30.06549370	1.9372	-41.1656	1.9363	-40.5127

5. CONCLUSION

In this study, microwave antenna designs were formulated as a multi-purpose optimization problem and then modeled. It is also expressed in terms of optimal solutions and change relations according to the geometric design parameters of the antennas. The algorithm has been successfully applied to obtain the optimum design values for the requested cost functions using the MOM technique. The primary part of this work is that we reduce the time spent on antenna simulation by modeling using an artificial neural network. By adjusting the hidden layers of the network and the number of neurons it contains differently and increasing the number of trained samples, the results of the ANN model can be improved. We have shown that ANN models can be used effectively in microwave antenna design by eliminating time-consuming and complex mathematical operations in antenna design.

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Chapter 6

AN OVERVIEW ON COLLOIDAL DELIVERY SYSTEMS IN FOOD INDUSTRY: ENCAPSULATION TECHNOLOGIES AND IMPLEMENTATIONS

Bilge ÇELIK [1]

Nil ACARALI [1,*]

1 Yildiz Technical University, Department of Chemical Engineering, Davutpasa Campus, 34210, Esenler-Istanbul, Turkey.

celikbilgee@gmail.com (https://orcid.org/0000-0003-0696-6976)

*nilbaran@gmail.com (https://orcid.org/0000-0003-4618-1540)

1. INTRODUCTION

The food industry has a very important place in the industry, as it produces nutrients, which is one of the most basic needs of human life. The food sector is enough to meet the demand for adequate and healthy food in parallel with population growth, which maintains this strategic importance. While food businesses produce products that have a direct impact on human health and performance, they must also consider that customer demands and expectations may change over time. Because, investments in products with short shelf life in food businesses create a stocking cost per day when the product cannot be sold, and bring the risk of product spoilage [1]. The food sector takes its raw material from the agricultural sector. For this reason, the agricultural sector and the food industry affect each other and develop in parallel in each country. The degree of interaction increases and/or decreases depending on the level of development. The food sector, which requires a system with intense effort, is directly related to the evaluation of agricultural products, the supply of raw materials to the industry, its contribution to employment and a balanced diet of the people and has a strategic importance in socio-economic terms in all countries in the world [2].

2. COLLOIDAL DELIVERY SYSTEMS IN FOOD INDUSTRY

Colloidal systems play an important role in the design of products with enhanced control of product functionality due to their small particle size (typically <1 μm) and the possibility to control their composition and surface properties [3]. As a result of important studies in food science in recent years, new research and analysis have been developed within the extent of food category distribution systems due to increase the constancy, bioavailability and controlled release of bioactive drugs or nutrients. These delivery systems have a number of benefits and drawbacks related to constancy, bioavailability, biodegradability, biocompatibility, and expenses [4]. The colloidal delivery system includes a wide range of distribution systems, from submicron emulsions to colloidal particles, liposomes and micelles [5]. Different colloidal systems can be created from many food components. The purpose of creating a colloidal system is to encapsulate micronutritients and nutraceuticals, inclusive emulsions, nanoemulsions, microgels, oil masses, vesicles, biopolymer nanoparticles solid lipid nanoparticles and microemulsions [6]. Implementation of bioactive ingredients in food products by micro/nanocarriers can provide more benefits than essential nutritional values on a health basis [7]. Functional performance of each of these distribution systems depends on structural and physicachemical properties such as particle size, morphology, stability, optical properties, rheology and sensory properties. Accordingly, the most appropriate colloidal application system should be selected and applied for each specific application according to the properties desired in the final product [8]. As shown in Figure 1, i) average dimensions, (if it is larger than 500 nanometers it is called microcapsule, if it is smaller than 500 nanometers it is called nanocapsule.), ii) grading of their structures as homogeneous and heterogeneous, iii) homogeneous and heterogeneous, iv) The physical property of the disperse system can be categorized as of liquid, liquid crystals and crystalline or noncrystalline solids [9].

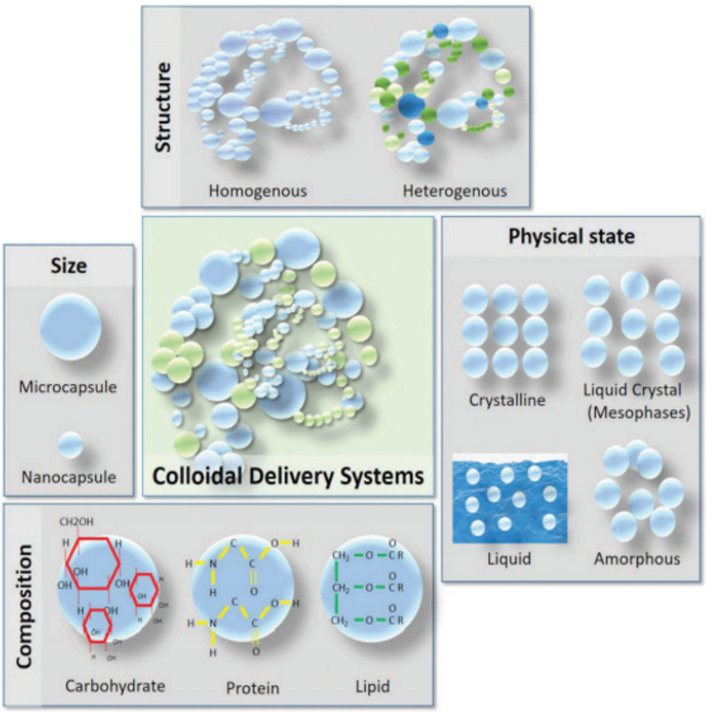

Figure 1. Classification of colloidal transport systems in different categories [9]

2.1 Encapsulation Technology and Nanotechnology

Encapsulation is particulary suitable technology for providing valuable products that can stabilize to release of high value-added compounds to products extracted from fruits, vegetables or waste materials [10]. It can also be defined as the mechanism in which a substance or a mixture of substances is covering or binded in another substance or form. In this form, the covered substance is called live or seed substance and the covering substance is called hull, carrier or encapsulant [11]. Initially, encapsulation has been used to make production processes more efficient to a rapid development of matrix-producing cells and metabolites around cells in the field of biotechnology. This technologies that developed about sixty years ago are great interest especially in the pharmaceutical and vaccine distribution parts of the pharmaceutical industry, but this also applies to the food industry. In these days, the food industry has necessitated the insert of operational compounds to outputs. These compounds are typically considerable tender to environmental, processing and gastrointestinal conditions, and thus encapsulation procures a closing to effectively preserve them [12]. Encapsulation process is applied for many different purposes. Some of the purposes are:

- Extending the shelf life by protecting sensitive food materials against environmental and processing conditions,
- Ensuring the release of food ingredients at the appropriate point of the digestive system,
- Increasing the bioavailability of food ingredients,
- Providing homogeneous mixtures when small quantities of use are required,
- Removing unwanted taste and odor and preventing reacting with other compounds of material to be covered,
- Facilitating the transportation and storage of the substance [13].

In the food industry, nanotechnology has been utilized to encapsulate nanoscale operations and components, for instance novel functional supplies, as well as to develop procedures and instrumentation to ameliorate food safeness, nutritional utility and biosecurity [14]. Since 1980 developing nanotechnology, it has provided both scientific and food industry, including the emergence of many innovations in industrial areas. Nanotechnology has been utilized to manufacture a various of food and potables (e.g. cream cheese, mayonnaise, puddings, bakery products) since it has been discoveried in the food industry [15]. Today, nanoencapsulation as an emerging area of nanotechnology involves the keep of bioactive substances, providing the targeted efficiency, increasing the resistance aganist thermal and mechanical stress, using less chemical and synthetic preservatives [14].

2.1.1 Nanoencapsulation Technologies

Nanoencapsulation technologies can be categorized in five parts according to the basic ingredient used to compose nanocapsules in the food industry. These are:

- Lipid-based nano-encapsulation,
- Nanoencapsulation originated by nature,
- Special equipment based nanoencapsulation,
- Biopolymer based nanoencapsulation,
- Other various nanoencapsulation methods.

Choosing of a suitable technology is very significant for the manufacture of food bioactive charged nanocarriers and in addition, it is based on numerous parameters. For instance, the aimed release profile and distribution objectives, physicochemical characteristics of the last output, economic situations, appropriate material, know how etc. [16].

2.1.1.1 Lipid based nanoencapsulation

Lipid-based nanoencapsulation bodies are very suitable carriers that are rapidly being developed for various purposes. However, lipid-based nanocapsulations can be applied on an industrial scale and provide low toxicity. Although there are different nanocarriers, the leading lipid nanocarriers include nanoliposomes, solid lipid nanoparticles, nanoemulsions and nanostructured lipid carriers [17].

- ***Nanoliposomes***

The successful application of liposomes has emerged to use of nanolipozom to encapsulation of sensitive bioactive compounds. Small size nanoliposomes compared to liposomes are used to express particle dispersion in the 10-1000 nm range. It makes bioactive compounds more active in the protection and transmission. The physical, structural, thermodynamic properties and formation mechanism of nanoposomes are the same as liposomes [18]. The nanoliposome formation that occurs by the simultaneous encapsulation of oil and water soluble molecules is shown in Figure 2.

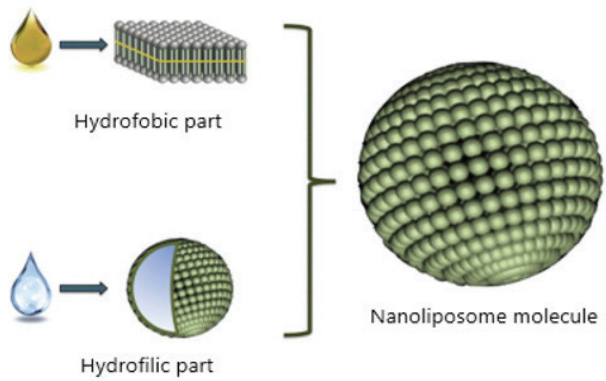

Figure 2. Nanoliposome formation by simultaneous encapsulation of water-soluble and fat-soluble materials [19]

- ***Nanoemulsions***

Nanoemulsions that a sort of colloidal dispersion, formed by dispersing dribbles of one liquid into particular unsent liquid. Characteristically, two liquids such as water and oil may be dissolved, yet other unsent liquids can as well create emulsions. There are two prevalent sorts of nanoemulsions that separated from one another by their chemical texture: oil-in-water and water-in-oil structures. The illustration of this example is given in Figure 3. [20].

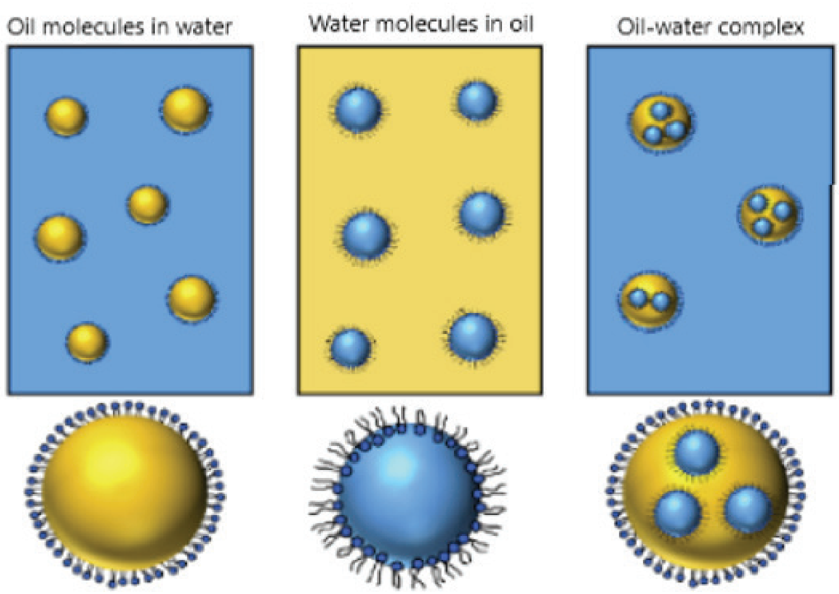

Figure 3. Oil molecules in water, water molecules in oil and oil water complexes [20]

In principle, a nanoemulsion consisting of oil and water can be formed without the use of a surface active agent. Efficaciously, this model is quite labile to dribble combination and it is necessary to enable nanoemulsion formation and ensure the kinetic stability of nanoemulsion in the course of storage. The apolar batchs of the surface active agent molecules adsorb into the hydrophobic core that creating by the oil phase, while the polar batchs of the surface active agents adsorb towards the enclosing hydrous phase [21]. Nanoemulsions are thermodynamically labile by reason of the essential rest energy to separate the oil phases from the water phases is minor by comparison the essential energy for the emulsification transaction. Therefore, nanoemulsions characteristically decomposed meantime they storage by the reason of multifarious processing that are sedimentation, flocculation, coalescence, and Ostwald ripening [22]. The kinetic consistency of nanoemulsions can be advanced by examining their microstructure or by inclosing substances that known as emulsifiers; texture modifiers, weighting agents or balancers such as maturation retardants [23]. Another potential advantage of nanoemulsions in certain applications is that they may look transparent or just a little blurry when they are synthesized to have shred magnitudes much lesser than the wavelength of light. The reason for this condition is that the shred magnitude is lesser than the wavelength of light. Therefore, they only poorly disperse light [24]. Figure 4 contains a visual of this situation.

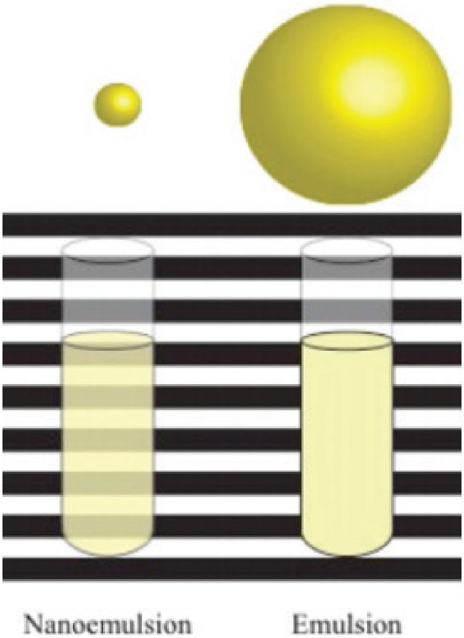

Figure 4. Appearance of emulsions and nanoemulsions [24]

- ***Solid lipid nanoparticles***

First generation lipid nanoparticles, called SLNs, have been acquired using a lipid matrix composed of solid lipids. These particles have a very regular flint glass pattern and are balanced by an outer onlooking of emulsifiers. It can also be manufactured from a uniform stiff sort of lipid or using a combination of lipid lots whose mobility is controlled by the physical lipid matrix state of the included compounds [25]. The drawbacks of solid lipid nanoparticles are that association and gelation composition of suspensions in manufacturing or stockpiling provisions. Solid lipid nanoparticles are especially formed from physiological lipids. These particles have many advantages that high chemical and physical steadiness, reformed bioavailability, continuous emission and beware of subsumed molecules responsive to environmental impacts [26]. Solid lipid nanoparticles are quite common and beneficial in food applications. Because many solid lipid-derived foods (e.g., hydrogenated palm oil, cocoa butter, anhydrous milk butter) consist of a congeries mixture of glycerides in various chain tallness [27].

- ***Nanostructured lipid carriers***

Nanostructured lipid carriers (NLC) are the most promising systems in connection with their high encapsulation productivity, higher colloidal steadiness depends on the higher consistency of the solid lipid, not require to harness structural diluents in its manufacturing, less tendency to particle shape changes [28]. NLCs enclose a favorable blend of solid and liquid lipids. While the solid lipid defends the lipophilic composits in case degradation, the liquid lipid assists to decompose of compound and officiates as a physical drawback counter detriment agents from the aqueous phases. Therefore, the assessment of solid lipid and liquid lipid proportions is crucial for the upgrade and comprehension of the specialities of nanosystems [29]. The important advantages of NLCs to be applied in food products are as follows:

➢ The provides more active area for encapsulation of bioactive substances.

➢ The provide a controllable release profile thanks to the solid matrix.

➢ The ability to protect encapsulated bioactive substances against external degradation conditions.

➢ Have a highly encapsulation productive and highly physical and chemical steadiness.

➢ The surface of NLCs can be exchanged with suitable polymers for various purposes, such as improving their stability or targetability [30].

2.1.1.2 Nanoencapsulation originated by nature

Nano and micro capsules can be formed naturally during some food processes. For example, casein micelles in milk encapsulate many components naturally. In addition, amylose chains bind some aromatic components during bread production and these components can only be released during baking. In addition to all these, natural cavities in some components, such as cyclodextrins, can be filled with various components and the encapsulated compounds are protected thanks to strong molecular interactions [13].

- ***Cyclodextrins***

Cyclodextrins (CDs), which serve as natural nano-carriers especially in the drug and food industries, are prevalent used in the nano-encapsulation of multiple distinct bioactive composits in order to improve their bioavailability, steadiness and some functional specialities [31]. Natural CDs can be used in food as admixtures and are "Ordinarily recognized as safe" [32]. CD's are α (1-4) glycosicly bonded, non-reducing, cyclic maltooligosaccharides obtained by cracking with cyclodextrin glycosyl transferase enzyme. The most widely used and known of cyclodextrins that named according to a good deal of glucose units They are α-CD, β-CD and γ-CD and composed of glucose molecules that six, seven and eight units respectively, sequentially (Figure 5). The cyclodextrin molecule has hydroxyl batches on the facing. In the intramolecular surface, there are hydrogen atoms and glycosidic oxygen bridges that have nonpolar properties. Therefore, the cyclodextrins, which are geometrically in the form of a 3-dimensional conical cylinder, have hydrophobic inner surfaces and hydrophilic outer surfaces [33].

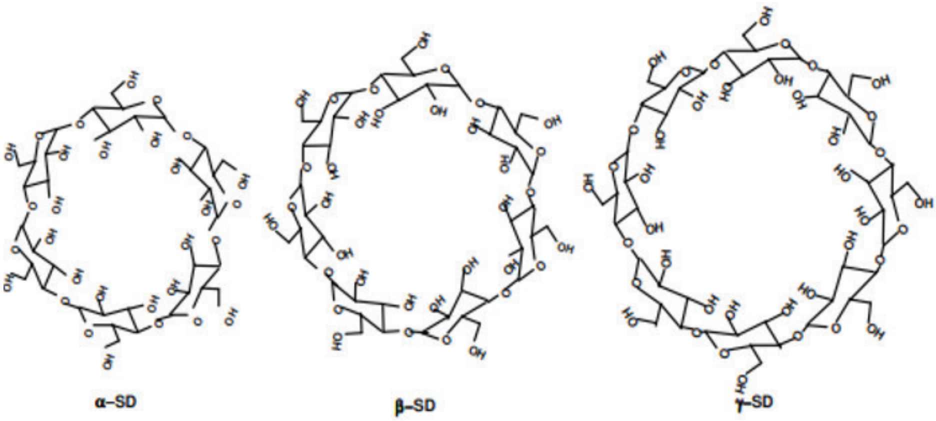

Figure 5. Chemical structure of α, β ve y- cyclodextrins [33]

- ***Casein***

Casein, as a large milk protein, is designed substance due to intensify, steady and relocate of essential nutrients (in particular calcium, phosphate and protein) for newborns. Clear majority of caseins in milk are formed on the part of micellas known as colloid corpusculars and defined as conglobate calcium phosphate colloids that have 50-500 nm diameter. Although many casein structures have been designed, caseins are held together thanks to hydrophobic interactions within the micelle, mainly [31]. The advanced encapsulation efficiency of caseinate and micellar casein has been studied by a lot of analysts and the structural properties of the casein micelle perform a cautious task in the encapsulation capability, especially the strong affinity and high oxidative stability. Caseins concatenate hydrophobic molecules through various sciences that consisting of hydrophobic interplays, van der Waals forces, and hydrogen bonding. Casein micelles have also been examined for their accomplishment to encapsulate β-carotene. Casein micelles have been shown to protect beta-carotene versus degradation even as the most widespread industrial treatments kind of pasteurization, high hydrostatic pressure, sterilization and baking [34].

2.1.1.3 Special equipment based nanoencapsulation

- *Emulsification:* Emulsification is the preferred method to encapsulate bioactive ingredients in aqueous solutions by forming nanoemulsions. Nanoemulsions are colloidal dispersions including two unmixable liquids; one of them diffuses into the other as droplets within the dimension interval of 50-1000 nm.

- *Coacervation:* It occurs as a result of sorrounding the core by forming a homogeneous layer around the core material of the coating phase associated with the separation from the polymeric solution of the liquid phase of coating material.

- *Creating inclusion complexes:* The iclusion complexing method refers to the ancapsulation to a substrate containing a cavity of an internal phase by means of hydrogen bonds, Van der Waals force, or entropy-oriented hydrophobic impact [35].

- *Emulsification-solvent evaporation:* It occurs two stages. In the first step, an emulsification process is implemented to and aqueous phase of polymer dispersion. In the second step, the polymer solvent is vaporized, which induces the composing sedimentation of the polymer as shaped nanospheres. [36].

- *Supercritical fluid technique:* This technique is used to encapsulate of susceptible components to heat in a analogous process that is spray drying. In this method, the bioactive part and polymer are lysed in the fluid and solution is enlarged by way of a nozzle. Subsequently, the supercritical fluid that is vaporized in the spraying method and at long last the lysed particles settle. This technique has extensive usage because it requires low critical temperature and marginal organic solvent access [35].

2.1.1.4 Biopolymer based nanoencapsulation

Biopolymer-based nanoparticles are described as submicron biopolymeric shreds that can utilized in order to nanoencapsulation of bioactive compounds [13]. Inherent macromolecules (chitosan, cellulose, etc.), man-made biopolymers and derived composite substances are basically used in antioxidant and antimicrobial encapsulation. Biopolymers that belonging food section such as polysaccharides, proteins or functional ingredients can be encapsulated. As a result of this process produce a particular nanostructures to nanofibers and various nanocomposites from nanolaminates [37].

2.1.2 Microencapsulation Technologies

Microcapsulation is identified as the procedure of fixing coating of delicate bioactive constituents and volatile in lipid shell or stable and flexible polymer on a micro scale. The microencapsulation technique applied in food chains can preserve bioactive constituents in the course of the processing and stockpiling of foods in order to the use of high temperatures and the absence of oxygen. Some labours have indicated that the implementation of microcapsules acquired with complicated coacervation in food systems increases the steadiness of bioactive constituents in the course of stockpiling [35]. Microcapsulation methods are divided into three groups:

- Physical methods (lyophilization, spray drying, solvent vaporization and supercritical liquid sedimentation etc.)
- Physico-chemical methods (liposomes, ionic gelation etc.)
- Chemical methods (interface polymerization etc.) [36].

2.2 Encapsulation Processes

Encapsulation technology has been used based on the principle of occuring an powerful fence toward peripheral factors such as luminary, oxygen and free radicals of liquid and solid materials in the food industry. Since encapsulation compounds are mostly in liquid form, most of them are hinged on desiccation processes [38]. There are many different techniques for encapsulating active substances. To illustrate, spray drying, fluid bed coating, melt extrusion, emulsification, freeze drying and co-extrusion etc. [38, 39].

2.2.1 Spray drying

Spray drying is a method in which a liquid output is pulverized in a hot gas stream to obtain an instant powder. Spray drying, which reduces water ratio and water performance, is constantly in order to get the microbiological steadiness of outputs, eschew the risk of chemical and/or biological deterioration, minimize stockpiling and carrying expenditures, as an end procure a certain output in the food industry [40]. In the spray drying method, the feeding solution send to the main drying section by a pump. In this section, the solution atomizes into droplets. However, the hot air feed to drying section. Particles which exposed to hot air lose their moisture. As a result of the spraying process, dried particles collect in the final product section and a powder product is obtained [41]. The representative of this process is given in Figure 6.

Performing encapsulation process with spray drying technique depend on significant parameters that production efficiency and physicochemical specialities of the last output, the temperature of the air that entering and outing the drying system, the kind and combination of the encapsulated substance, the flow rate of the drying air and the feed temperature [41].

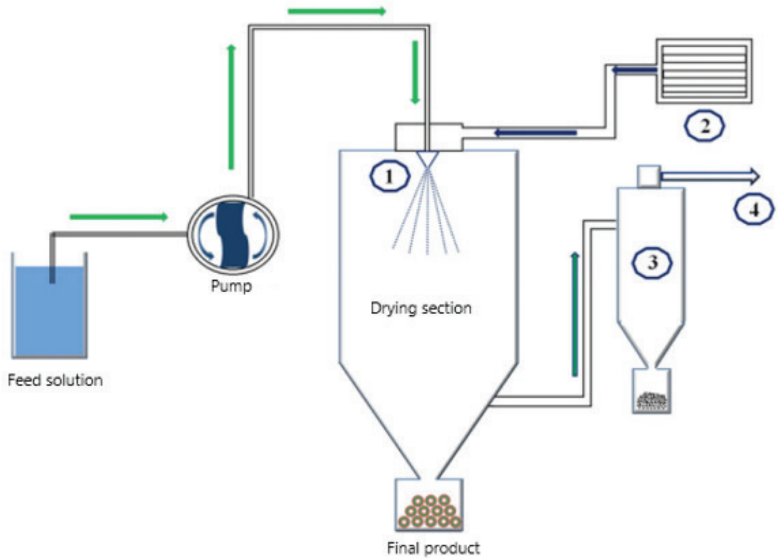

Figure 6. Representative scheme of spray drying mechanism 1) repelling, 2) air warming regulation, 3) cyclone distinguishing, 4) stack air [41]

2.2.2 Hot melt extrusion

Extrusion is the process that changing the physical properties of a material by passing it through a hole or a die under controlled conditions [42]. Hot melt extrusion (HME) is a deep seated industrial system that utilized in the manufacturing of comestibles (eg meat, creams, snacks, cheese, cornflakes etc.). As a result of this process, a product that has improved solubility, dispersion and stability features, is obtained. One of the most important advantages of this process is that hot melt extrusion has a aliasing on certain antinutritional agents in crude substances that are protease inhibitors and lectins susceptible towards thermal processing [43].

2.2.3 Fluid bed coating

The method, conventionally utilized for pharmaceutical applications, has present an crucial procedure in the food industry over time. In the fluidized bed coating process, solid microparticles that dimensions are between 50 -1000 micrometer in suspension moving upward from the floor of the reactor are encapsulated by way of the heated air stream n the part of an air diffuser. The hydrous plating stuff is atomized in blobs of 10-40 micrometer with a nozzle positioned above the fluidised bed that functioned at a defined atmospheric pressure. Both solid particles and plating stuff blobs as they get around wherein the bed, replace mass and heat transfer with the atmosphere inside the bed and internal boundary of the reactor. As the operation proceed, the plating dispersion recurrently wets the area of the solids and desiccates and by this way the core stuff is covered. The demonstration of this process is given in the Figure 7 [44].

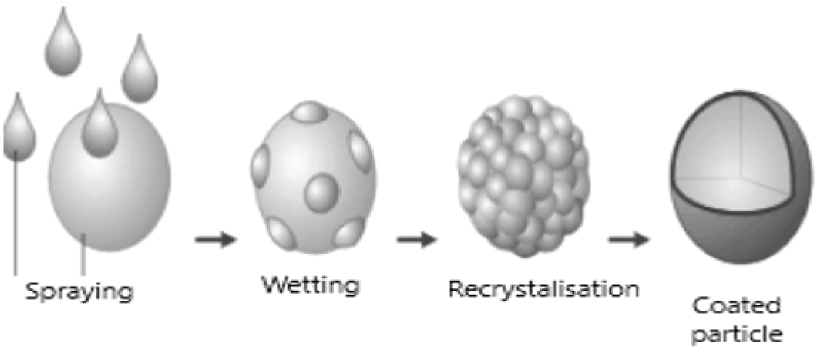

Figure 7. Process steps of fluid bed coating [45]

2.2.4 Freeze drying

The freeze-drying mechanism of food consists of two basic stages: freezing and drying [46]. Freezing is the first stage of desiccation of by freezing and therefore it is a crucial stage in specifying output standard. The majority of the water during freezing is transformed into a solid state, forming a network of ice crystals. This step determines the ice crystal morphology, dimension and dimension distribution. Sublimation desiccation that ordinarily kenned prime drying, describes the conversion to steam phase of a solid phase, by which skips the intermediate liquid phase. When the primary drying is complete, all of the frozen water is sublimated. Primarily the adsorbed water diffuses to the surface of the solid from the interior matrix of an amorphous solid to the area of the solid. Later the water vaporizes from the solid area and steam is carried through of the desiccated output to the ice concentrator [47]. The process has specific implementation, for example; freeze-dried coffee, freeze-dried vegetables and freeze-dried sea cucumber, etc. in the food industry. However, the freeze-drying process is certain extent limited due to its high costs in foods. The freeze drying process consists of extremely costly equipment. Considering all the stages of the freeze-drying process, it is concluded that the energy consumption is too high [46].

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