مجلة غريان للتقنية

مجلة علمية محكمة تصدر عن المعهد العالي للعلوم والتقنية غريان

غريان - ليبيا

العدد الثالث مايو 2018

مجلة غريان للتقنية Gharyan Journal of Technolgy 2018

Gharyan Journal of Technolgy

Annual, Corrected and Accademic Journal

Issued By

Higher Institute of Sciences and Technology, Gharyan

Gharyan Journal of Technology

Annual, Reviewed and Academic Journal

Issued By

Higher Institute of Sciences and Technology, Gharyan.

To Contact Us:

Telephone : 0913506053

E-mail: ghjt2016 @ gmail.com

Contents

Hazard Identification and Risk Assessment for a Refrigerated Propane Storage Tank- Part A

Abdunaser S. Aljabri

Department of Chemical Engineering, Higher Institute of Science and Technology, Al-Garraboli, Libya.

الملخص

الغرض من هذه الورقة هو تطبيق تقنيات تقييم المخاطر على خزان البروبان المبرد الذي يمثل جزءا من وحـــدة استعادة الغاز الطبيعي المسال وذلك بهدف المساهمة في جعل عمليات التشغيل آمنة قدر الإمكان. تبدأ الورقة بوصف عام للعملية مع ذكر بعض الحوادث القديمة الهامة و التي هي مشابهة ومتصلة إلى حد ما إلى العملية قيد الدراسة، ومن ثم اجـراء التحليل الذي يركز على سلسلة من التقنيات التي تكشف عن أهمية عمليات السلامة.

ان الطرق المستخدمة في هذا البحث صنفت طبقا لاستخدامها، على سبيل المثال، تقنية دراسات المخاطر والتشغيل (HAZOP) وهـي تقنـية اساسـية لتحـديد وتقيـيم المخـاطر بالإضـافة إلى ذلك تستخدم طرق أخرى مـثل (Risk Ranking/Matrix) و(Human Errors) بينما ((Fault Tree Analysis (FTA) و (Event Tree) تكون تقنيات مركزية لتحليل احتمالية تكرار المخاطر. ولقد تم اختيار طرق أخرى مثل (Jet fire) و (Vapour Cloud Explosion (VCE)) لتوضيح العواقب وتوسيع نطاق الآثار الناجمة عن حدث غير مرغوب فيه. وتسلط الدراسة الضوء أساسا على الحاجة إلى تقييم المخاطر في الصناعات الكيميائية. وحيث انه من الصعب تغطية كل هذه الطرق و التقنيات في ورقة بحثية واحدة، لهذا قرر تقسيمها إلى جزئين. وفي هذا الجزء (أ) سوف يتم مناقشة تقنيات تقييم المخاطر بينما سيخصص الجزء الثاني (ب) لتغطية تقنيات احتمالية تكرار المخاطر والنتائج.

ABSTRACT:

The purpose of this paper is to apply risk assessment techniques on a propane refrigerated storage tank which represents a part of LNG recovery plant at Gdansk, Poland with the aim to contribute in making the operating processes as safe as possible. The paper starts with a general description of the process and considers some important past incidents that are similar and related to some extent to our process, and then conducts the analysis which is focused on a series of techniques that reveal the importance of safety and safety analysis.

These methods were grouped according to the issues that they are investigating. For example, Hazard and Operability Studies (HAZOP) is the basic applied hazard identification technique in addition to Risk Ranking/Matrix and Human Errors whereas Fault Tree Analysis (FTA) and Event Tree are central techniques for a frequency analysis. Other methods such as Vapour Cloud Explosion (VCE) and Jet fire are chosen to illustrate the consequences and extend of impacts due to an undesired event. The study basically highlights the need for risk assessment in chemical process industries. However, since it is impractical to cover all these techniques at once, it has been decided to group them into two parts. In this part A, the hazard identification techniques are discussed whereas part B will be devoted for covering frequency and consequence analysis techniques.
Keywords: Hazard Identification; Hazard and Operability Studies; Risk Ranking/Matrix; Human Errors.

1. INTRODUCTION

The history of chemical process industries has reported several major incidents that ended up with major hazards. These major hazards came mainly to include fire, explosion and toxic release. Although fire is found to be the most common type among the others, explosion is particularly significant in terms of fatalities and loss. Toxic release, however, has perhaps the greatest severity as it can kill a large number of people and lead to long-term toxic impact on the area. The tragedy scenario at Bhopal, India 1984 works as a achieve example for such a release. The avoiding of such disasters, therefore, is basically dependent on avoiding loss of containment [1].

The causes of such loss of containment, however, can be direct as in rupture in lines, vessels or valves left open, or indirect as in a release due to runaway reaction caused by a release through piping and vessel rupture or pressure relief devices. All these issues put safety and its importance into great account. Generally, most industries consider workers safety while operating on-site, nevertheless a good management policy should also take off-site safety and general public into account[2].

Therefore, lessons from past incidents can be of great assistance in identifying major factors leading to accidents. A survey of these disasters showed that 1744 significant incidents were occurred during the period 1928-1997, with 441 accident (5%) involved fires and explosions, and 1247 (71%) involved toxic release. Most of these accidents dealt with LPG and LNG operations. Propane, in particular, have found to be the chemical product in around 12 accidents resulting in many deaths and injured. Table (1) illustrates the locations and the details of propane accidents occurred worldwide [3].

Table (1): List of major propane accidents.

Year	Location	Chemical	Event	Death/ injured
1962	Ras Taruna, Suadi Arabia	Propane	Fire	1/11
1966	Feyzin, Farnce	Propane	Fire & Explosion	18/83
1972	Lynchburg, VA	Propane	Fire	2/3
1973	Kingman, AZ	Propane	Fire	13/89
1973	St. Amand. L'Eaux, France	Propane	Explosion	5/45
1974	Decatur, IL	Propane	Explosion	7/152
1975	Eagle. Pass, TX	Propane	Fire	16/7
1978	Waverly, TN	Propane	Explosion	12/21
1984	Roeoville, IL	Propane	Explosion	15/76
1985	Mont Bolyiey, TX	Propane	Fire	4/13
1988	Narco, LA	Propane	Explosion	7/48
1990	Porto de Leixoes, Portugal	Propane	Fire & Explosion	14/76

Based on reported data in the literature of process industry, operations which involve storing hydrocarbons in refrigerated storage tanks are less potential for fire or explosion. Most of the past incidents, on the other hand, were associated with materials stored within pressurized storage tanks. Accordingly, it could be argued that refrigerated tanks are more practicable since they are capable to store large quantities of hydrocarbons at low temperature and atmospheric pressure.

This conclusion, however, draw the reader to state that the proposed storage tank is "*inherently safer*", but hence does not mean that hazards are unlikely to arise from such tanks. The reported incidents for major leak fro a 20,000 m^3 liquefied propane tank in Qatar in 1977 is an achieve example of incidents involved refrigerated storage tanks. The consequences of the leakage, as reported, were seven deaths and extensive damage to the rest of the plant due to the fire and explosion that were raised after the leak has been ignited. It was also reported that the propane leak has occurred twice at the same tank but in the earlier year it did not ignite.

The learnt lesson from Qatar incident is that instead of having a company policy which mainly focuses on how to prevent cracks; a rather sufficient policy can be reached by relying on the crack-arresting properties of the tank material. Hence, it has been recommended that refrigerated LPG tanks should be constructed from materials, such 9% nickel steel, which do not allow for crack propagation. Moreover, the force which allowed liquefied propane to escape from the crack led to its spillage over the dike wall. One of the limitations of conventional dike walls is that large amount of material can be exposed to the atmosphere once leakage occurs. Due to these limitations, the modern adopted practice is to support the cryogenic storage tanks with a circular concrete wall jacket built about 1m away from the main wall. These walls, however, should be designed to be constructed from materials that can withstand any sudden release. Such findings, in turn, would give plausible justifications for the selection of double containment as the proposed storage tank of this study [4].

2. SYSTEM DESCRIPTION

The current storage system that is in investigation represents a part of an LNG natural gas recovery plant located in Gdansk, Poland. In this plant hydrocarbons; methane, ethane, propane, butane and gasoline are recovered separately by introducing these materials through three main stages where certain treatment producers are applied to them in each stage. A simple block diagram illustrates these sections is given in Figure (1) [5].

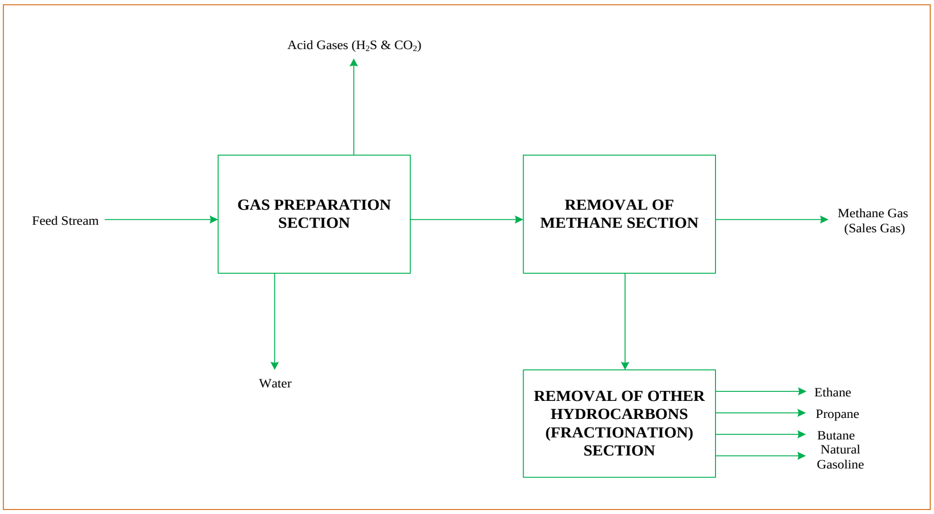


Fig.1. The three main stages for LNG fractionation

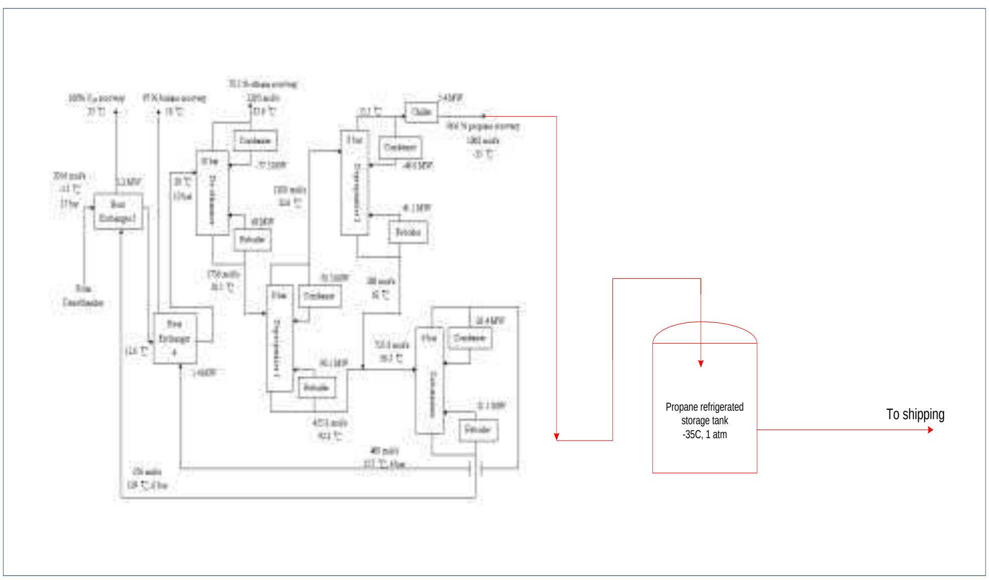


Fig. 2. Fractionation flow process diagram applied at LNG Recovery Plant.

The propane is stored within double containment tanks which are designed and constructed so that both the inner and outer tanks are capable to independently contain the stored refrigerated liquid. Such type of tanks store the refrigerated liquid in the inner tank under normal operation conditions, whereas the outer tank is designed to contain the refrigerated propane that may leak from the inner tank. But the outer tank is not capable to contain any vapour resulting from propane leakage from the inner tank.

Furthermore and based on the flow rate of liquid propane from the chiller (1000 mole/s), the tank needs around two days to be fully filled, and accordingly the shipping comes every two days to unload the tank where another spare tank is also provided [7].

3. STORAGE HAZARDS

Prior to start the safety analysis, it would be beneficial to have a glance over the potential storage hazards in the chemical industries. That is to say determining the kind of hazards associating with storage tanks is mainly depending on the nature of the stored materials as well as the type of the storage. A vessel or a tank can experience failures of different degrees extending from overpressure and underpressure failures to catastrophes due to mechanical or metallurgical defects. Filling storage tanks too rapidly can also cause overpressure conditions whereas underpressure conditions are potential when tanks are emptied too rapidly [8].

However, a release is another credible hazardous scenario associated with storage tanks that has the potential to cause fatalities. Such a problem may occur as a result of failures in equipment, pipework and/or fittings. In terms of equipment, pumps are seemed as a type of equipment with a great tendency to leak. On the other hand, a release from pipework can be a consequence of crack pipehole, a full bore rupture, or a failure or a leak at a flange, valve or gasket.

Release may also occur due to major incidents such as explosions which are potential at different scenarios as in the case where a tank that may burst due to being exposed to overpressure that cannot withstand. Nevertheless, explosion may also happen due to the ignition of flammable mixture or evolution of gas due to the reaction of different components such as impurity and material of construction. The other cause of release that should be considered is having a runaway reaction with the vessel or the tank. Additionally, fire is another important factor that should be considered as one of the factors leading to tank failures. This might involve a jet fire or a fire beneath the tank [9].

Although overfilling is another operational activity during which a release can occur, draining, sampling operations and maintenance practices are other operational activities which are regarded as potential causes of release. Moreover, loss of containment from storage can happen due to impact events such as the impact from a carried item, a dropped load, or a vehicle. However, natural events such as high winds, flooding, rainstorms and earthquakes may also lead to loss of containment whilst lighting may be a source of fire. In what follows, there will be a discussion of the importance of the applied methods in this study.

4. JUSTIFICATION FOR THE APPLIED TECHNIQUES

Hazard and Operability Studies (HAZOP) was chosen to be the primary used method for hazard identification through which a list of problems were identified and accompanied with suggestions for system improvement. And because of this important role, it was thought necessary to start our analysis with this technique which has the privilege of flexibility and allows freedom for creativity. Another valuable advantage of using HAZOP method is that its results can form the input to a probabilistic safety assessment, as the input to develop operating procedures, and as the basis for design change. Also, conducting a HAZOP study improves the safety quality by making people more aware of potential hazards and by keeping up-to-date instructions [10].

Besides, despite the similarities between HAZOP, FMEA and What-if techniques, HAZOP is preferred as it involves a vessel by vessel and pipe by pipe review of the plant. In this study, HAZOP is used to identify a major flammable release of propane from the tank as the most serious hazard. This release, in turn, represents the top event that will be developed in Fault Tree Analysis (FTA) in Part B of this study.

Moreover, Risk Matrix is adopted after HAZOP as a means to rank the potential hazards according to their severity. Based on

Risk Matrix results, proper and reliable mitigation measures have to be considered for events with high severity and likelihood.

However, since undesired hazardous events are still potential even when equipment and control systems are working properly, human errors is thought to be another important hazard identification technique which may lead to undesired events and hence will be covered here [11].

5. HAZOP TECHNIQUE

One of the advantages of HAZOP technique is that it considers all possible ways through which hazards and operating problems may occur. The conduction of HAZOP study on the process was based on the proposed flow diagram for a refrigerated storage tank which is shown in Figure 3 below.

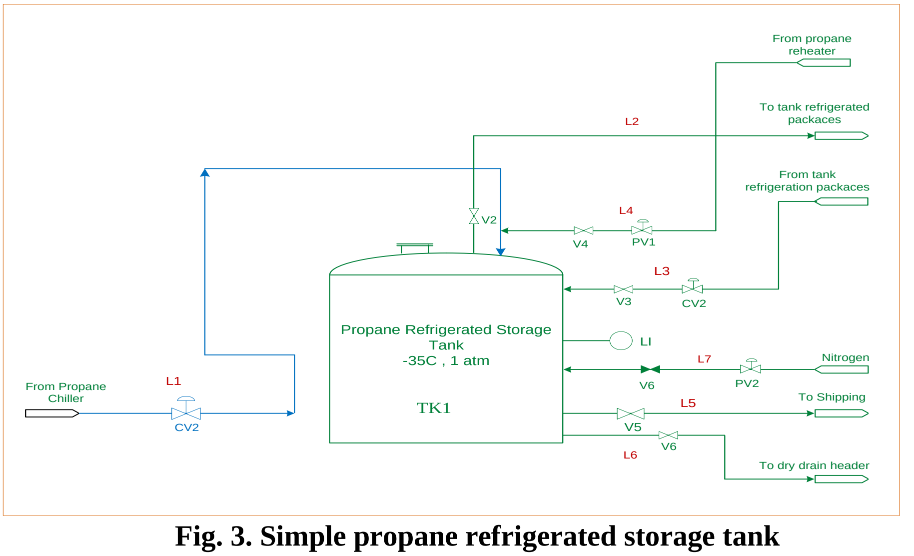


Fig. 3. Simple propane refrigerated storage tank

The modification has involved the installation of additional instrument as follows:

A. Line 1 (L1)

1. Local pressure gauge
2. Install isolation valves and bypass at CV1
3. Provide integrating flow meter

4. Install high high level alarm linked to CV1.
5. Install nonreturn valve
6. Install propane reheated line (L4) with pressure controller and ressure low low linked to pressure valve.

B. Propane storage tank (TK1)

1. Pressure indicator with high/low alarm linked to control room.
2. Local pressure gauge.
3. Level indicator with high/low alarm linked to control room.
4. Temperature indicator with high/low alarm linked to control room.
5. Local temperature gauge.
6. Vacuum relief valve.
7. Electrical heat at the base of TK1.
8. Pressure relief valve.
9. Outer tank or wall.

C. Line 2 (L2)

1. Pressure controller with high/low.
2. Pressure valve.
3. Isolation valves and bypass at PV2.

D. Line two (L3)

1. Isolation valves and bypass at CV2.
2. High level control linked to CV2.
3. Nonreturn valve.

E. Line 4 (L4)

1. Isolation valves and bypass at PV1.
2. Install pressure controller (PC1) and low low pressure (PLL) linked to PV1.

F. Line 5 (L5)

1. Sampling point.

G. Line 7 (L7)

1. Pressure controller linked to pressure valve.
2. Nonreturn valve.

Reasons for the modifications

- Having integrating flow meter installed on the liquid line (FQ).

  The installation of the integrated flow meter on liquid propane feeding line (L1) should be done in a systematic way; it should not be installed prior to installing CV1. This is because in the event of having closed control valve, different reading will be recorded on the meter. Therefore, in the scenario of having FQ deviation such as low/no flow, it will be possible to detect the leakage source, equipment failure, and blockage and/or pipe rupture. It is also a good practice to ensure regular checking of FQ readings by the operator and this is normally stated within the operating procedure of the company.

- Installing remote pressure indicator to the TK1.

The installed pressure indicator should be linked to the control room to ensure it will be monitored by the operator and will not exceed the allowed range. But it is also required to install high and low pressure alarms beside the pressure gauge to ensure any undesired conditions will be observed in the event of operator's incautiousness.

- Installing remote temperature indicator to TK1.

The installation of this equipment will enable the operator to monitor the inlet temperature of liquid propane and detect any deviations that are about to occur. For example, the temperature for liquid propane should be kept at $-35C^0$.Therefore any increase or decrease in the temperature may cause problem.

- Installing local pressure indicator in TK1 and L1.

The point behind having local pressure indicator is to observe how exactly the operation is running in the storage tank. It makes it possible for the operator to monitor the pressure inside L1 and TK1, and takes the appropriate actions once changes in the pressure are detected. Regular checking of the pressure should be clearly stated in the safe operating procedures.

- Installing local temperature indicator.

Local temperature indicator is the means by which the operator ensures that the temperature of the tank shows compliance with the planned operation modes. There will be a record for any deviation to ensure it will not obstruct the system.

- Isolation valve and bypass at each valve (CVs) or (PVs).

The point of having isolation valve is more to do with the scenario of control valves and/or pressure valves failures and where maintenance work is required. Bypass should be provided at each valve to be used once failures occurred.

- Sampling connection.

Checking the quality of the stored liquid propane cannot be done without having analyzer and sample connection fitted on the tanks. Sample connection should be installed on line 6 (L6) to detect any potential problems such as leakage that may occur during operation and detect any damage inside the tank.

- Install pressure controller and pressure low on propane reheated line.

The aim beyond having this action is to ensure control of the storage pressure and temperature once they dropped more than the required level. In the event of having low operation conditions due to the chiller impact, the pressure controller, as it is designed to work as low low pressure, will send a signal to open pressure valve and allow propane reheated to escape with liquid propane feed.

- Vacuum relief valve.

It means of a final vacuum protection. But if the pressure of the tank dropped further, nitrogen and reheated propane are injected into the tank.

- Relief valve.

A BOG compressor re-liquefying the BOG from the tank is mostly used during normal operations to ensure the pressure of the tank does not exceed the desired range. But in the event of tank unloading, it is possible to record an increase in the pressure where the pressure relief valve is opened to the atmosphere as a final protection method.

- Electrical heat at the base of TK1.

This heat is installed to avoid ice formation in the earth especially that the temperature of the liquid propane is low.

- Outer tank or wall.

It is important to ensure that any leakage of the liquid will not accumulate under the tanks. Hence, outer tank or wall is fitted to contain the refrigerated liquid product leakage from inner tank.

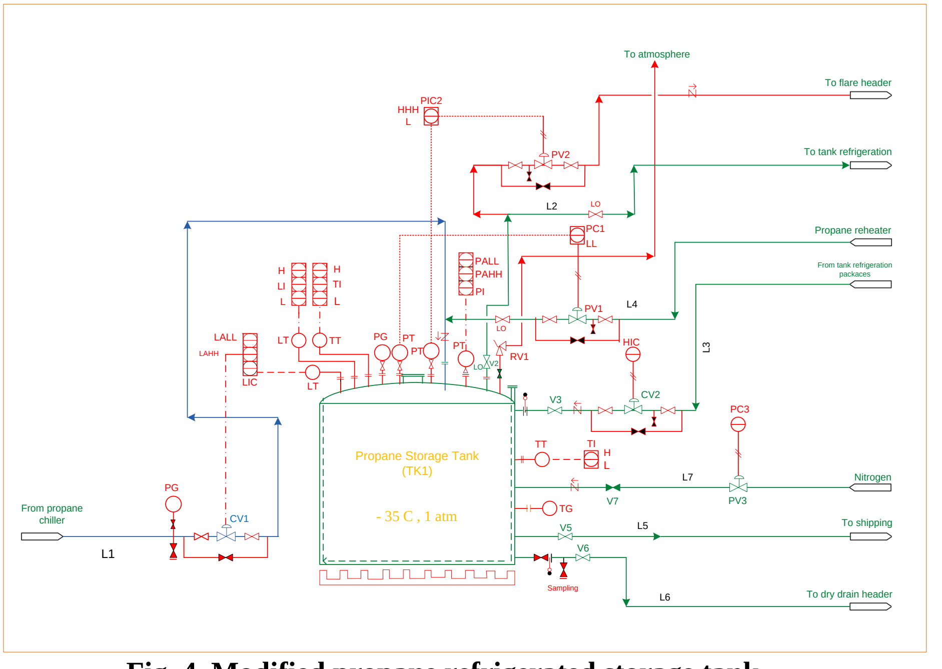


Fig. 4. Modified propane refrigerated storage tank

As a result of HAZOP, several modifications were proposed to the storage tank diagram in order to make it safer. A modified diagram is given in Figure (4).

6. Risk Ranking/Matrix

Risk matrix is another hazard identification method which reflects the importance of risk management strategies during conducting risk assessment for any particular company. It works by rating the levels of risk of all potential events. Risk value is determined by estimating of the potential severity of hazardous event and the likelihood that it will occur. Risk value is formulated as:

$$R = P * S$$

Where:

P= Likelihood of occurrence

S= Potential severity of harm

Table (2): Categories for Likelihood

Frequent	E	5
Probable	D	4
Remote	C	3
Not likely	B	2
Improbable	A	1

Table (3): Categories for Severity

Severe	V	5
Very serious	IV	4
Serious	III	3
Moderate	II	2
Minor	I	1

Table (4): Risk Rating Criteria

Category of Risk	Evaluation of tolerability
Low (Level 3,4)	Risks that should be reduced so that they are tolerable or acceptable (unwanted)
Medium (Level 6,8,9,10)	Risks that should be reduced so that they are tolerable or acceptable (unwanted)
High (Level 12,16)	unacceptable

Applying the risk rating for Leak from L1, CV1

R= P * S

R= 4 * 4 = 16 (The risk level is unacceptable).

Risk matrix was applied for the propane refrigerated storage tank in this process and the technique was conducted following the way stated in [12] and this can be seen bellow.

Table (5): Risk Ranking Calculation

	Cause	**Likelihood**	**Severity**	Risk	**Number**	**Severity**
1	Equipment failure before L1	C	I	Low	3	I
2	L1 blockage/ rupture	C	IV	High	12	IV
3	CV1 fails shut	D	II	Medium	8	II
4	Operator incorrectly closed CV1	C	II	Medium	6	II
5	CV1 fully open	D	IV	High	16	IV
6	Excess flow of propane from chiller	C	IV	High	12	IV
7	CV1 partially open	D	I	Low	4	I
8	Leak from L1, CV1	D	IV	High	16	IV
9	Partial blockage in L1	C	II	Medium	6	II
10	Same as 5					
11	External fire	B	V	Medium	10	V
12	Same as 8					
13	Same as 11					
14	More temperature from supply	C	III	Medium	9	III
15	Ingress of impurities into L1 such as butane or pentane	B	III	Medium	6	III
16	Solids in line 1such as (wax, sand scale, salt and hydrate)	B	II	Low	4	II
17	Rupture due to lightning, earthquake or impact of aircraft).	C	IV	High	12	IV
18	Same as 1					
19	Same as 2					
20	Same as 3					

21	Same as 4					
22	Same as 5					
23	Storage tank leakage or partially blockage	C	IV	High	12	IV
24	TK1 not filled properly- Human error	C	I	Low	3	I
25	Drain header valve (V6) fails open.	C	II	Medium	6	II
26	Operator leaves V6 open	C	II	Medium	6	II
27	Same as 8					
28	Increase level in the storage tank and V2 not opening	B	III	Medium	6	III
29	CV2 fails shut	D	II	Medium	8	II
30	L2 blockage or V2 fails to open	C	III	Medium	9	III
31	Same as 5					
32	Same as 11					
33	Low pressure from chiller	C	III	Medium	9	III
34	Less temperature from chiller	C	III	Medium	9	III
35	Less temperature at TK1 bottom	C	III	Medium	9	III
36	Same as 15					
37	Nitrogen valve (V6) leaks to liquid propane inside TK1	C	II	Medium	6	II
38	Poor construction material selection	C	IV	High	12	IV
39	Loss of electrical power	C	II	Medium	6	II
40	Loss of air	C	II	Medium	6	II

The table illustrates the variation in scoring amongst different incidents. The most hazardous events are those which recorded the highest scores in the index. Although the incidents no 2, 5, 6, 8, 10, 12, 17, 19, 22, 23, 27, 31 and 38 have the highest scores, incidents no 11, 13 and 32 will have the highest consequences.

However, despite having "severe" consequences for the incidents no 11, 13 and 32, they represent low risk since they are unlikely to occur. The scores have been plotted on the risk matrix diagram as follows:

Plotting the incidents on risk matrix diagram enabled us to speculate that five incidents (1, 7, 16, 18 and 24) are in the acceptable region (the green part). Apart from these particular incidents, all the other incidents are subject to analysis to draw those in acceptable region or as low as reasonably possible (ALARP) region. So after conducting risk matrix, one can say that some of the operations associated with propane storage tank are severe and potential to cause serious fatalities. Therefore, it is worthy applying safety analysis to this part of the process to avoid any undesired scenarios.

	Broadly acceptable region. Need to maintain assurance that the risk remains in the region.
	Tolerable only if risk reductions are impracticable or cost is disproportionate to improvement gained
	Unacceptable region. Risk cannot be justified except in extraordinary circumstances.

V	Severe		11, 13, 32			
IV	Very serious			2, 6, 17,19, 23, 38	5, 8,10,12, 22, 27, 31	
III	Serious		15, 28, 36	14, 30, 33, 34, 35		
II	Moderate		16	4, 9, 21, 25, 26, 37, 39, 40	3, 20, 29	
I	Minor			1, 18, 24,	7	
		Improbable	Not likely	Remote	Probable	Frequent
		A	B	C	D	E

Fig. 5. The risk matrix diagram of the propane storage tank.

In addition to equipment failure, operator's incautiousness or failure may lead to undesired events.

1. HUMAN ERROR

Most of the literature on human error has cited it as a main cause and contributing factor in the past incidents. Three Mile Island, Bhopal, Flixborough and Chernobyl are examples of such incidents that occurred due to latent errors. Bhopal tragedy, in particular, involved multiple errors and human act of neglect, misunderstanding and omission as work supervisor observed a leak in one of the storage tanks but mistakenly they assumed it water leak and accordingly the required action was delayed which led to some problematic events.

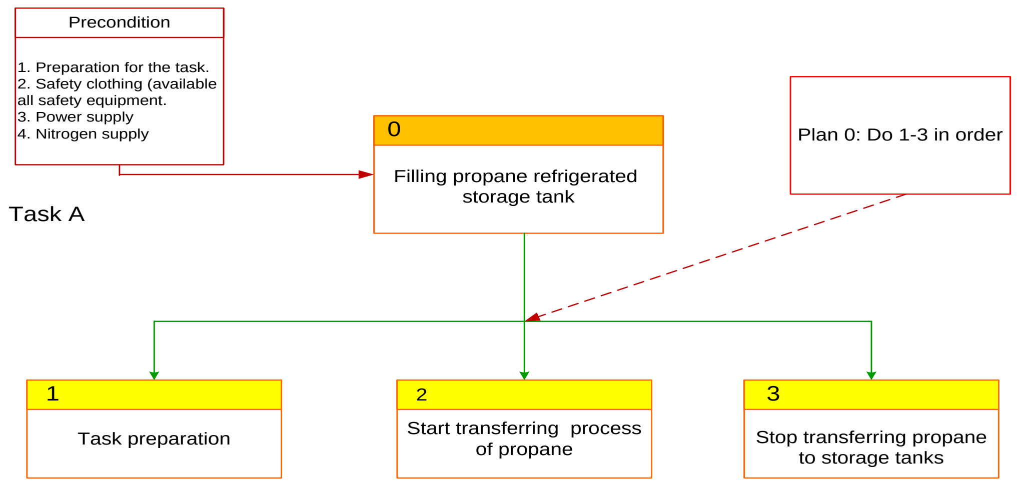
Also, improper cleaning of water from the tank led to an exothermic reaction. Therefore, human awareness and knowledge is critical issue that should be considered to ensure safe operating systems.

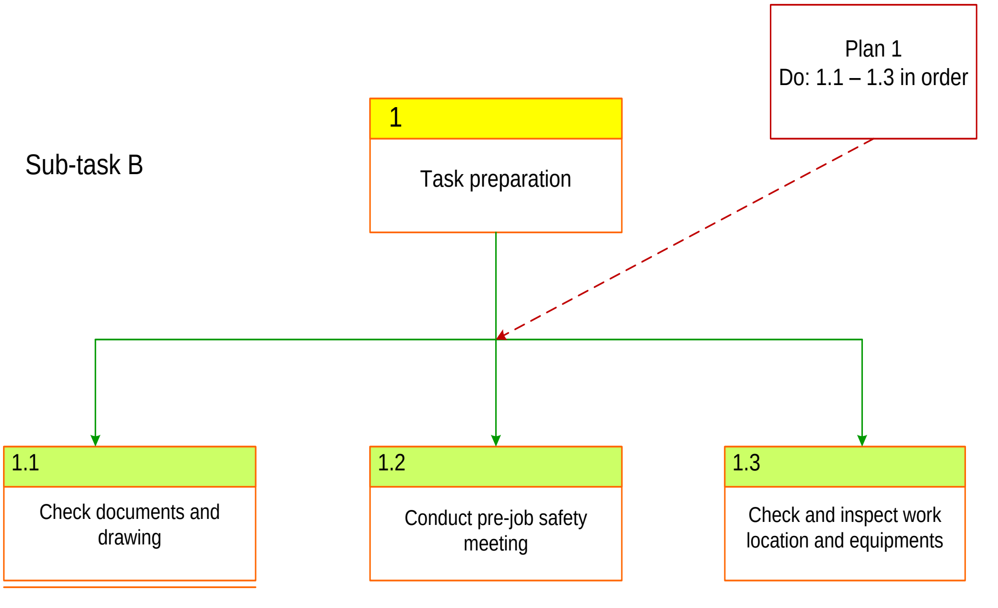
However, determining the causes and contributing factors in human errors is something of equal importance [13]. A table shows the contribution of human performance problems is provided below:

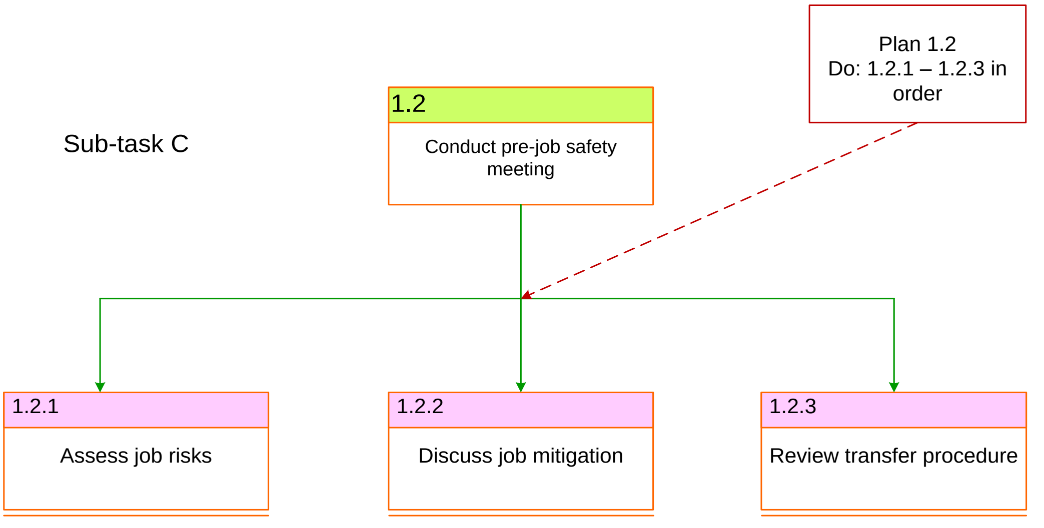
Table (6): Breakdown of human performance problem

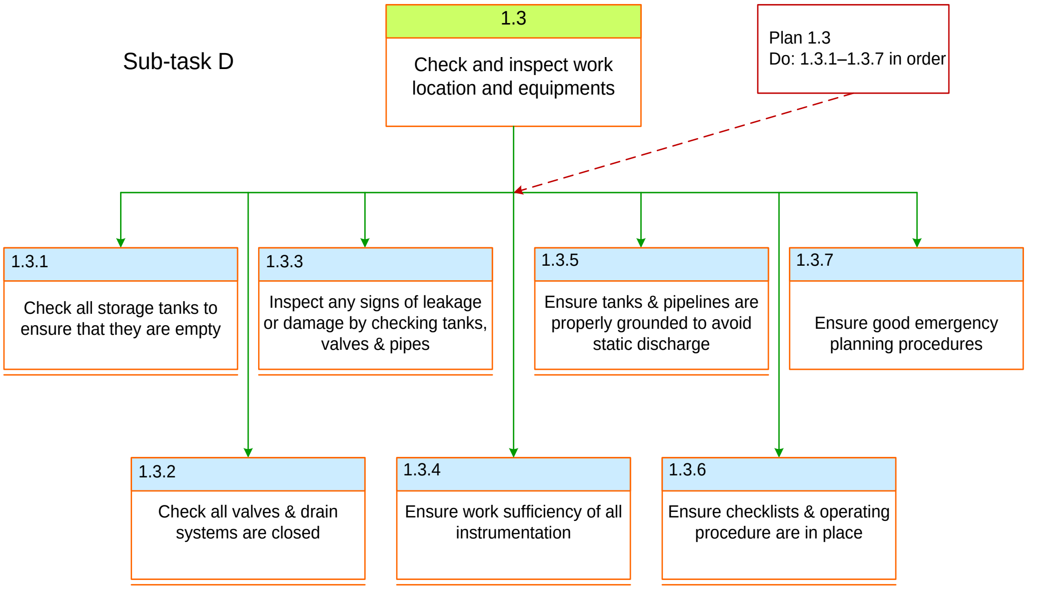
	Human performance problems
43%	Deficient procedures or documentation
18%	Lake of knowledge or training
16%	Failure to follow procedure
10%	Deficient planning or scheduling
6%	Miscommunication
3%	Deficient supervision
2%	Policy problems
2%	Other

In regards to our process (storage tank), overfilling of the tank is one of the most frequent consequences of operator error that may lead to fire or explosion. Overfilling may occur in scenarios when the operator forgets to close the manual valve after the liquid reached the required level or in the event of level measurement failure. Other mistakes associated with storage operation would have been forgetting to empty the spare holding tank and/or having inoperative refrigeration system (e.g. kept shutdown to save costs). A systematic illustration of the main and sub-tasks involved in filling the storage tank with propane is provided in what follows.


Precondition
1. Preparation for the task.
2. Safety clothing (available all safety equipment.
3. Power supply
4. Nitrogen supply
Task A
0
Filling propane refrigerated storage tank
Plan 0: Do 1-3 in order
1
Task preparation
2
Start transferring process of propane
3
Stop transferring propane to storage tanks


Sub-task B
1
Task preparation
Plan 1
Do: 1.1 – 1.3 in order
1.1
Check documents and drawing
1.2
Conduct pre-job safety meeting
1.3
Check and inspect work location and equipments


Sub-task C
1.2
Conduct pre-job safety meeting
Plan 1.2
Do: 1.2.1 – 1.2.3 in order
1.2.1
Assess job risks
1.2.2
Discuss job mitigation
1.2.3
Review transfer procedure


Sub-task D
1.3
Check and inspect work location and equipments
Plan 1.3
Do: 1.3.1–1.3.7 in order
1.3.1
Check all storage tanks to ensure that they are empty
1.3.3
Inspect any signs of leakage or damage by checking tanks, valves & pipes
1.3.5
Ensure tanks & pipelines are properly grounded to avoid static discharge
1.3.7
Ensure good emergency planning procedures
1.3.2
Check all valves & drain systems are closed
1.3.4
Ensure work sufficiency of all instrumentation
1.3.6
Ensure checklists & operating procedure are in place

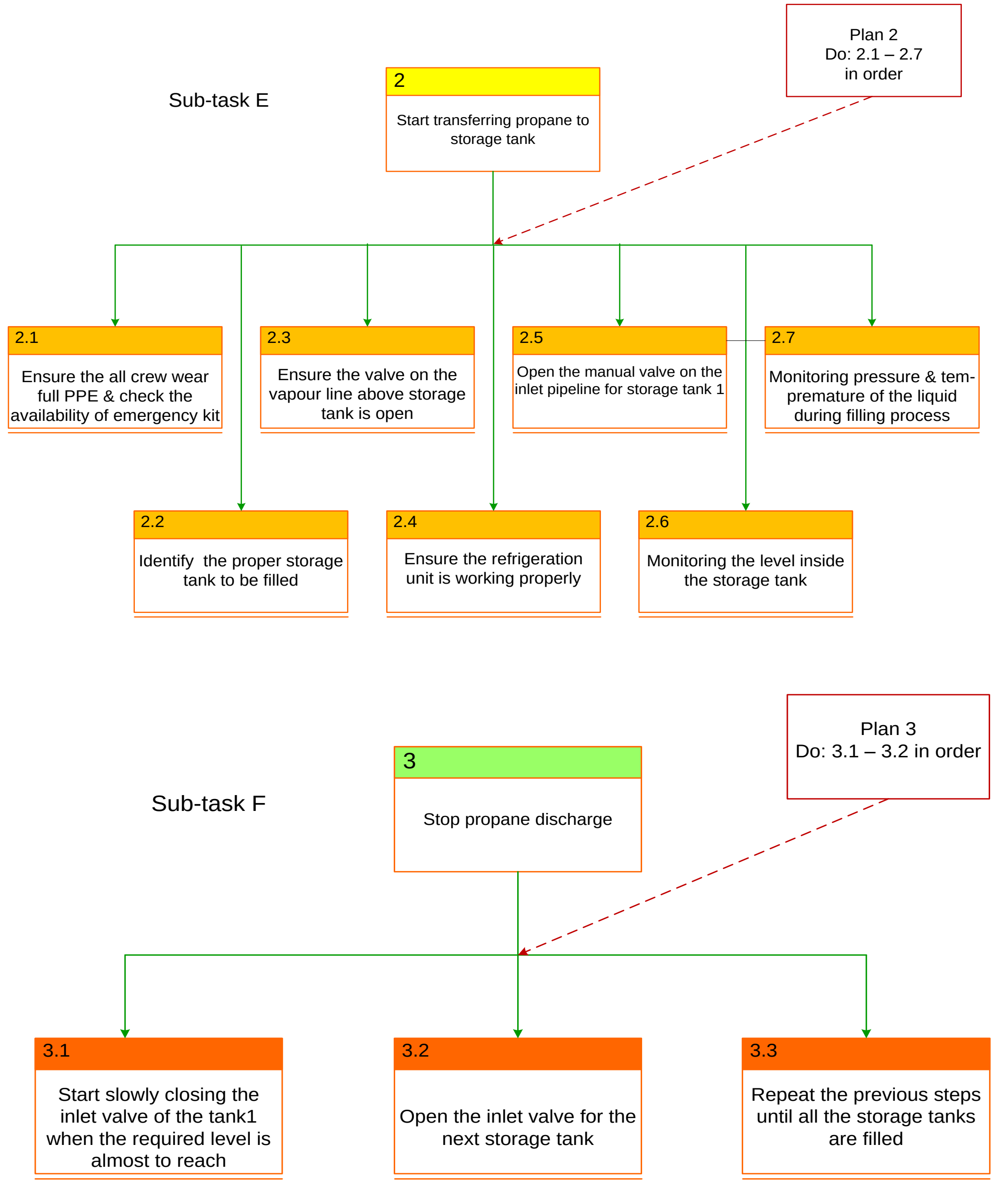


Fig. 6. Tasks involved in filling the propane storage tank.

8. CONCLUSION

This paper has provided some standards to analyze the risk assessment of a propane storage tank. The analysis has covered a selection of hazard identification and risk assessment techniques that are thought to be suitable and reliable for studying this part of the plant. As it has been explained from the qualitative risk assessment, it results that the risk of a major accidents (1,3,4,7,9,16,18,20,21,24,25,26,29,37,39 and 40) are acceptable , being necessary a periodical monitoring and a strict operational system. The biggest risk of a major accident belongs to incidents (2,5,6,8,10,12,17,19,22,23,27,31 and 38).Incidents (15,28 and 36) has a reduced risk because of the probability of occurrence, but the consequences can be significant and these scenarios can not be ignored. Incidents (11, 13 and 32) also include medium risks, but the consequences of such accidents can be severe if they are not managed immediately by the operating personnel.

Both of working equipments and operators should work in combination to ensure smooth working processes and hence to avoid any undesired problem or incident. Over all, great concerns should be given to the critical hazardous events associated with propane storage tanks, and their possibility to cause fatalities.

REFERENCES

[1]. Marshall, V. C., 1987. Major Chemical Hazards. England. Ellis Horwood Limited.

[2]. Lees, Frank. P., 1996. Loss Prevention in the Process Industries. Vol(1). Great Britain. Butterworth-Heineemanm.

[3]. Khan, Faisal I., Abbasi, S. A., 1999. Major Accidents in process industries and an analysis of causes and consequences. Journal of Loss Prevention in Process Industries. vol. 12. Pp. 361-378.

[4]. Kletz, Trevor., 2009. What when wrong? Case Histories of Process Plant Disaster and How They Could Have Been Avoided. Oxford. IChemE.

[5]. LNG Recovery Plant Design Project. Poland, 2008. The University of Sheffield.

[6]. API Standards., 1998. Venting Atmospheric and Low-Pressure Storage Tank. Nonrefrigerated and refrigerated. Fifth edition. American Petroleum Institute.

[7]. Skellton, Bob., 1997. Process Safety Analysis: An Introduction. UK. IChemE.

[8]. Lees, Frank. P., M. L.Ang., 1990. Classification of Hazardous Locations. UK. Institute of Chemical Engineering.

[9]. Lees, Frank. P., 2005.Loss Prevention Industries. vol (3). Oxford. Butterworth-Heinemanm.

[10]. Hoepffner, L. 1989. Analysis of the HAZOP study and comparison with similar safety analysis systems. Gas Separation and Prification vol.3. (3). pp 148-151.

[11]. Wells, Geoff., 2004. Hazard Identification and Risk Assessment. UK. Institute of Chemical Engineering.

[12]. Cox, L.T, 2008. What's Wrong with Risk Matrices?. Risk Analysis.vol28.P 497-502.

[13]. Peters, Barbara. J., 2006. Human Error Causes and Control. United States.

Human's Fatigue Detection System Based on Eyelid Blinking

Salaheddin Salama Sayeh[1], Mohamed Mostafa burkhiss[2], Abdelhamid emhemed aboujlida[3]

[1]Faculty of Computer Technologies, Tripoli-Libya, [2]Faculty of Computer Technologies, Tripoli-Libya, [3]Faculty of Computer Technologies, Tripoli-Libya

Abstract*:*

This paper describes method for detecting the early signs of fatigue in person. As soon as the person is falling in symptoms of fatigue immediate message will is transfer to the supervisor in any place due to any sever medical problems. The fatigue system is detected based on eyelid blinking. The mechanism is based on detects face, eyes and tracks the eyes for the person. Based on eyelid blinking, along with templates that monitor how long the eyes are open or closed. Tests of the approach were run on many persons to find its potential and its limitations. The system is very efficient to detect the fatigue. The results confirm that our method is able to measure human fatigue and show the validity of the proposed approach. Moreover; it can be used for vehicles driver and medical area.

Keywords: Fatigue, Human's drowsiness, Driver fatigue.

Introduction

The word fatigue is used in everyday living to describe a range of afflictions, varying from a general state of lethargy to a specific work-induced burning sensation within one's muscles. Fatigue is a phenomenon that influences a person's ability to perform a task on various levels. Fatigue defined as a state in which performance capabilities are temporarily impaired by continual activity demands which exceed the ongoing capacity to restore performance capabilities. [1] Fatigue can be defined as the feeling of tiredness, exhaustion or lack of energy to perform tasks in an efficient manner. This can further be categorized as physical or mental fatigue. Although physical fatigue can be addressed by refraining from performing the strenuous activity, the onset of mental fatigue is hard to detect. Table 1 lists the different types of fatigue detection methods that can help in these situations. [2]

Table 1: Classification of fatigue detection methods.

S.NO	Method type	Measured quantity	Applicability
1	Visual detection using camera	Eye closure and head motion	Driving or other operations that requires worker to be seated in constant position such as in cranes , etc.
2	Heart rate based methods	ECG	Generic
3	Muscle activity based methods	EMG,EOG	Worker performing physically intensive tasks
4	Brain wave based method	EEG	Generic
5	Psychomotor monitoring based methods	Movement of hand or limbs while performing tasks such as driving	Driving can be adopted to other operations were motion parameters can be monitored

When a worker is tired or deprived of sleep, there is natural tendency for the eyes to close. This can be analyzed using a camera. Active illumination imaging system is used to measure the eye closure in day light and dark conditions. The face region is analyzed to detect closure of eyes to estimate PERCLOS measure which gives an indication of fatigue. The cost of fatigue is of increasing concern to organizations across the globe as fatigue-related accidents and losses are extremely high. [3]

When a person's alertness is affected by fatigue, his or her performance on the job can be significantly impaired. Impairment will occur in every aspect of human performance (physically, emotionally, and mentally) such as in decision-making, response time, judgments, and countless other skills. The threat to safe aviation operations arises from the impairment to alertness and degradation of performance. [4]

This paper presents a system that measures the fatigue in human based on eyelid blinking. The system works with inexpensive USB cameras and runs at a frame rate of 30 frames per second. To prove this system's features, usability evaluation have been done through a laboratory experiment design. The experimental results have demonstrated feasibility of the concept and system. Therefore, this research will be a solution to address some human's fatigue problems such as vehicles accident and heavy transportation driver such as pilot.

The paper is organized as follows: section II is about the related work which summarizes previous researches on the fatigue techniques. Moreover section III provides more information about proposed system concept design and implementation. Section IV about evaluation where section V describes results and discussion. Section VI presents the conclusions.

Related work

The word fatigue is used in everyday living to describe a range of afflictions, varying from a general state of lethargy to a specific work-induced burning sensation within one's muscles [2].

Several of fatigue detection and monitoring system have been proposed, each has its own features.

This section analyses previous work on face and eye detection, eye tracking and eye state classification area.
Possible techniques for detecting fatigue in person can be broadly divided into four major categories:

- Methods based on human's current state, relating to the eye and eyelid movements [5].
- Methods based on human performance and human behavior [6].

• Methods based on physiological signals [7].
• Methods based on combination of the multiple parameters [8].

There has been lots of literature on detection of fatigue effects and the person's current state specifically focused on changes and movements in the eye. Generally, eyes detection consists of two steps: Locating face to extract eye regions and eye detection from eye’s windows several researches use Haar-Like feature and AdaBoost algorithm for detecting face and eyes and use PERCLOS to evaluate driving fatigue. PERCLOS (Percent Eye Closure), a video based method that measures eye closure is a reliable and valid determination of a driver’s alertness level. PERCLOS is the proportion of total time that the driver’s eyelids are closed 80% or more and reflects slow eyelid closures rather than blinks. For example Viola and Jones [9] have used boosted cascade of features to detect particular object. Template matching and support vector machine based approach is used to detect eye from face image [10] [11]. Eye-tracking is an area of computer vision that has been researched in the past years. The eye-tracking systems can be used for several applications. Some of them have already been implemented to conduct psychological studies about attention and interest [12]. [13] Describes the most important application of eye tracking i.e. driver drowsiness detection. In [14] float boost learning for classification is described. In [5] detected face and eyes region using Haar-Like feature and AdaBoost algorithm and used an improved template matching method to detect eye states and selected PERCLOS to evaluate driving fatigue. They used the transition of eyes state to detect eyes’ blink.

DESIGN STEPS OF FATIGUE DETECTION SYSTEM

The block diagram of fatigue detection system is shown in figure 1, which illustrates the whole system. The first stage of block diagram is data input source, which are classified by two methods for data input. The first method may be video file stored in the computer for human. The second method for input data to the system is by using web camera connected directly to computer. The second block is fatigue system which constitutes form many stages. The fatigue system is based on software that will analysis data input in many steps as shown below and last stage is output result in message appears on computer as fatigue state or not.

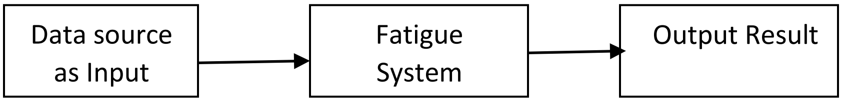


Figure 1 Shows block diagram of system

➢ PROPOSED FRAMEWORK

The construction of the framework is based on the derivation of every single component. It is done by mapping all components into a framework as illustrates in Figure 2. From Figure 2, the human's fatigue system is based on eyelid blinking algorithm. The end result will give the conclusion whether the human exhibits a fatigue or not. This systematic framework is developed as a guide to build a prototype using Matlab programming language software.

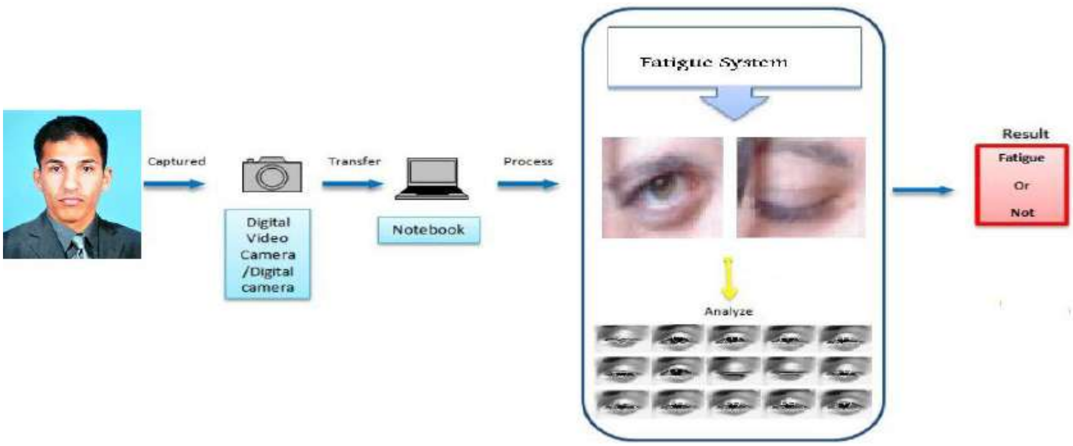


Fig 2 Framework of Human Fatigue.

➢ PROGRAMMING OF FATIGUE SYSTEM

The flow chart of basic components programming of Fatigue system are shown in figure 3 where will be discussed later in more detail for every step.

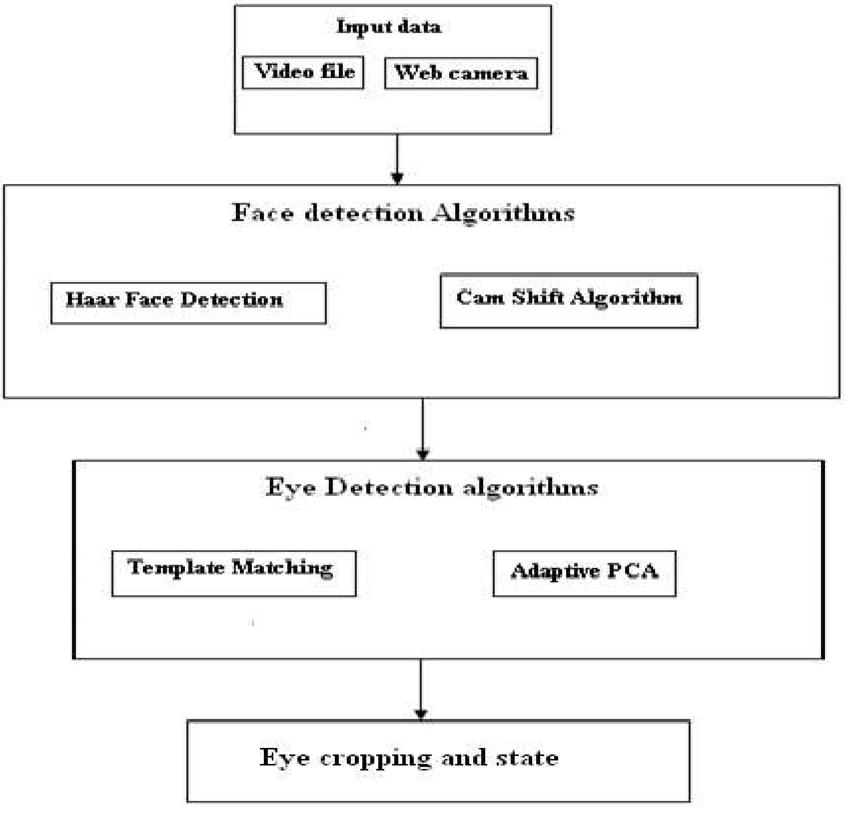


Figure 3: Block diagram of Fatigue system

➢ Face detection algorithms

The main working of the system is when the system gets started it firstly recognize the region of face which includes eye lids and eye ball positioning. Under supervision user of the system through graphic user interface it must be applied one algorithm as shown in figure 4. There are two algorithms used to detect face *Haar Cascade Classifier algorithm* and *Cam shift algorithm.*

For face detection it preferred to use Haar classifiers algorithm. These classifiers are based on features extraction, which are found to be contrast in variation inside a set of pixels making two distinguish areas, darker and lighter shades. The classifiers are prepared with two groups of images, good and bad examples of the specific features. To increase the accuracy of the system the proposed algorithm uses different Haar filters which make the face detection step more robust. For the purpose of minimizing the chances of errors and reduce processing time, relevant regions are cropped for further processing.

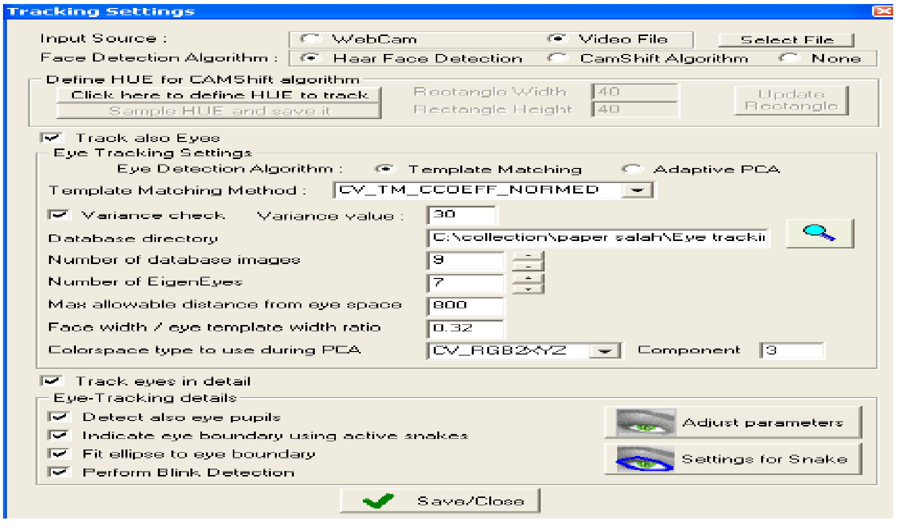


Figure 4 Shows Tracking setting configuration

➢ Eye detection algorithm

There are two algorithms for eye detection and tracking, where these algorithms are template matching and adaptive principle component analysis (PCA). Under supervision user of the system through graphic user interface it must be applied one algorithm as shown in figure 4. When chosen template matching for eyes detection and tracking in the option of GUI then the choice gives option to choose one of known standard template. The result of this choice is shown in Figure 7.

➢ Eye Cropping and state

After successfully detection eye, now the software system will crop an eye from detected image in separate windows as shown in figure 8. The detection of eyes status is very important. It is done by another small program out the software system. To measure the state of eye use algorithm implemented in Math Lab. In the Matlab software, the process begins with Image processing eye extracted from software system. The process is converts the grayscale image to binary image. The binary image consists of only two gray levels, where"0" represents Black and "1" represents White as shown in figure 9. In this the object eye balls are assigned white pixel value and background is assigned with black pixel. The number of white pixels is counted by program. If the value exceeds some fixed value then eyes are open otherwise eyes are closed, after that the end result will visualize whether the human is fatigue or not.

Results and Discussion

The system is tested on Video captured through USB camera. The graphic user interface GUI for the software system after tested is shown in figure 5.

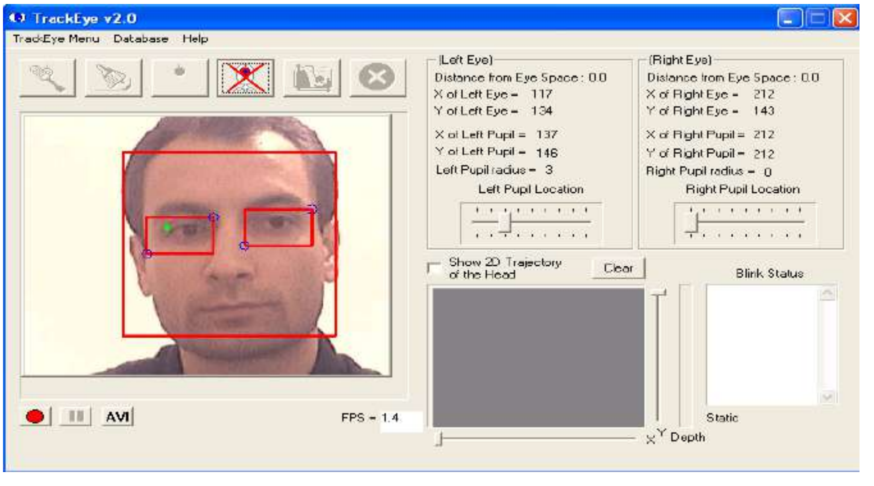


Figure 5 shows the GUI of the application where applied in the project.

The results are from software system. Use Haar classifier as face detection From GUI for the system and template matching for eye detection. This software system can detect the face, track the eyes. For functional testing, there is setting in coding for compute state of eye that if expected output of number of white pixels comes within range then it can be output state of person otherwise having functional fault. These settings of data can be varied for different persons.

Figure 6 shows result of face detection by Haar algorithm

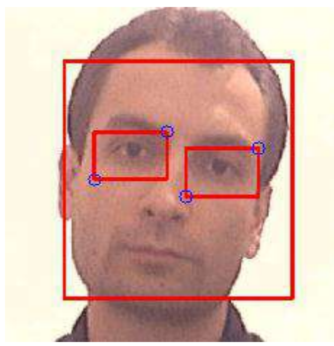


Figure 7 shows result of eye detection by template algorithm

Figure 8 shows result of eye cropping

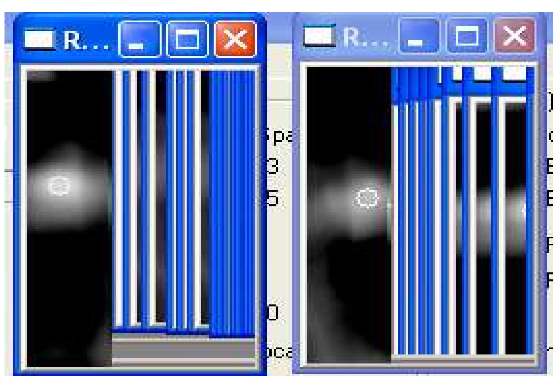


Figure 9 Shows results of Binary eye image

Conclusion and Future Work

A technological solution in human's life is important to address some human's behavior such as fatigue. In this paper, a framework for measurements of human's fatigue level by using one factor is proposed. This framework is more accurate measurement of human's fatigue level instead of another method based on medical instrumentation.

Based on this framework, the developed simulation can measure the human's fatigue level using eyelid blinking. Once the simulation has been developed, it can be adopted to develop a prototype via FPGA. The prototype can be used for accident prevention and safety for transportation and also for educational area.

References

[1] Vinod Pathangay & Aparna Kumpatla. " Fatigue Detection Technology for workers",2015

[2] P. Viola and M. Jones, "Rapid object detection using a boosted cascade of simple features", Proceedings of IEEE Computer Society Conference on Computer Vision and Pattern Recognition, **(2001)**.

[3] Harini Veeraraghavan,Nikolaos P. Papanikolopoulos"Detecting Driver Fatigue Through the Use of Advanced Face Monitoring Techniques",ITS Institute Center for Transportation Studies University of Minnesota(2001)

[4] Rosekind, Mark. (2011). Human Fatigue in Aviation Operations. Alertness Solutions Inc. retrieved on 15th January, 2011 from http://www.alertness-solutions.com/index.html.

[2] Q. Wang, "Eye location in face images for driver fatigue monitoring", Proceedings of the 6th International Conference on ITS Telecommunications, **(2006)**.

[5] Q. Wu, B. X. Sun, B. Xie, and J. J. Zhao, "A perclos-based driver fatigue recognition application for smart vehicle space," in Proc. 2010 Third International Symposium on Information Processing (ISIP), 2010, pp. 437–441.

[6] W. S. Wijesoma, K. R. S. Kodagoda, and A. P. Balasuriya, "Road-boundary detection and tracking using ladar sensing," IEEE Transactions on Robotics and Automation, vol. 20, no. 3, June 2004.

[7] M. A. Li, C. Zhang, and J. F. Yang, "An EEG-based method for detecting drowsy driving state," in Proc. 2010 Seventh International Conference on Fuzzy Systems and Knowledge Discovery (FSKD), 2010, pp. 2164-2167.

[8] J. J. Wang, W. Xu, and Y. H. Gong, "Real-time driving danger-level prediction," Engineering Applications of Artificial Intelligence, pp. 1247–1254, 2010.

[9] P. Viola and M. Jones, "Rapid object detection using a boosted cascade of simple features", Proceed-ings of IEEE Computer Society Conference on Computer Vision and Pattern Recognition, **(2001)**.

[10] Q. Wang, "Eye location in face images for driver fatigue monitoring", Proceedings of the 6th Internation-al Conference on ITS Telecommunications, **(2006)**.

[11] Kinjal Joshi, "Automatic Human Eye Localization and Its Validation for 2D Facial Image" Journal of BIOINFO Computer Engineering, vol.3 no.1, **(2014)**, pp. 60-62

[12] O. Oyekoya and F. Stentiford, "Exploring human eye behavior using a model of visual attention", Pro-ceedings of International Conference on Pattern Recognition, **(2004)**.

[13] Y. Du, Peijun Ma, X. Su and Y. Zhang "Driver fatigue detection based on eye state analysis ", Pro-ceedings of 11th Joint Conference on Information Sciences, **(2008)**.

[14] S. Z. Li, ZhenQiu Zhang, Heung-Yeung Shum and HongJiang Zhang, "FloatBoost Learn-ing for Classification", Microsoft Research Asia- http://research.microsoft.com/~szli

The Physical Methods Technique to Detection of Extra-Solar Planets

Khiria Ali Almaghrbi

Tripoli University- Faculty of Education Gaser Ben Ghashir

الخلاصة

تهدف هذه الورقة إلى توضيح بعض الطرق الفيزيائية المستخدمة لاكتشاف كواكب خارج المجموعة الشمسية . يطلق اسم كوكب خارج النظام الشمسي على أي كوكب يوجد خارج نطاق المجموعة الشمسية ، أي كوكب يدور حول نجم آخر غير الشمس ، وقد تم اكتشاف وجود معظم تلك الكواكب بطرق غير مباشرة ، وليس برؤية مباشرة لها لأن قربها من نجم ساطع يجعل رؤيتها بشكل مباشر صعبة جداً ، الأمر الذي أدى إلى تطوير عدداً متنوعاً من التقنيات القادرة على اكتشاف العديد من الكواكب الموجودة خارج نظامنا الشمسي ، ومن هذه الطرق الأساسية المستخدمة لذلك : طريقة عبور كوكب ، طريقة العدسية الصغرية الجذبية ، طريقة زمن النباض ، وطريقة مطيافية دوبلر وتسمى كذلك طريقة السرعة الشعاعية (القطرية). وتعتبر طريقة مطيافية دوبلر (السرعة الشعاعية) الطريقة الأكثر نجاحاً في الكشف عن كواكب خارج المجموعة الشمسية ولا تزال الطريقة الأكثر فعالية.

Abstract

This paper aims to clarify some of the physical methods used to detect extra-solar planets. An exo-planet or extra-solar planets is a planet outside of our solar system that orbits a star. Most of these planets have been discovered indirectly, because their proximity to a bright star makes seeing them directly very difficult. This has led to the development of a variety of technologies that can detect many planets outside our solar system. There are principal techniques which are used: Transit photometry, Gravitational micro-lensing, Pulsar timing and Doppler spectroscopy. Doppler spectroscopy technique is the most successful so far in finding extra-solar planets. It is still the most effective method for detecting exo-planets from Earth.

Introduction

Extra-solar planets or exo-planets are planets orbiting stars other than the Sun. The first detection was confirmed in 1992, with the discovery of planets orbiting the pulsar PSR B1257 +12 (Wolszczan, et al., 1992).

The decades since, astrophysicists and astronomers across the globe have developed an array of methodologies to discover many more of these extra-solar worlds. As these discoveries continue to dominate the scientific headlines and push the limits of observational astronomy, it is important for the non-astro-centric fields of physics to understand the scientific backbone supporting these discoveries (Glaser, 2015).

The first confirmation of an exo-planet orbiting a main-sequence star was made in 1995, when a giant planet was found in a four-day orbit around the nearby star 51 Pegasi. Since the first detection of planets outside the solar system, the number of discovered exo-planets has grown rapidly. To date, more than 1800 exo-planets have been confirmed (Uljan, 2015). The techniques that have been used to accomplish those discoveries and to study the properties of the exo-planets are based on physical phenomena (Lunine, et al., 2009).

The smallest exo-planets are a few times larger than the Earth, and many are several times larger than Jupiter. The fact that most of these planets are so much larger than Earth is thought to be because more massive planets are currently easier to detect than small ones (see ref. [8] http://www.physics.org).

Direct evidence of exoplanets is very difficult to obtain (see ref. [9] http://lasp.colorado.edu). This is because they shine not by their own light, but by light reflected by the star which they orbit. As a consequence, they are much dimmer than their parent star (in the case of Jupiter, for instance, by a factor of 100 billion), and any attempts to detect them by their own light are doomed to failure. Therefore, indirect methods must be used to find extra-solar planets. All of these methods rely on the fact that a planet exerts a small influence on its parent star as it travels around its orbit. By observing changes in the parent star, the existence of the planet can be deduced. Since the changes become larger as the planet becomes more massive, it is always easier to detect Jovian planets than to detect terrestrial ones (see ref. [13] http://www.astro.wisc.edu).

Methods

1. Transit photometry

The transit method for detection of extr-asolar planets is based on the detection of stellar brightness variations, which result from the transit of a planet across a star's disk. This method is also known as the photometric or occultation method (Hans-Jörg, 1998). When a planet passes in front of a star, the planet will block a tiny amount of light. Telescopes can detect this slight dimming and can work out the radius of the planet by how much light is blocked and the orbit by how frequently the planet passes in front of the star. One drawback is that a star needs to have the right orbit so it passes in front of the star . With this method we measure the brightness drop of a star, which results from the transit of one of its planets across its disk (figure1) (Uljan, 2015). This method can determine the radius of a planet, semi-major axis of the planetary orbit and inclination of the orbital plane of the planet. When combined with radial velocity data, a transit can also provide a good estimate of the planet's mass. The orbital period of a planet discovered using transit photometry can be found by measuring the time delay between one eclipse and the next. The principal problem with the transit photometry technique is that it only works for those extra-solar systems which are viewed edge on. Since this configuration is rather unlikely, only a few planets have been discovered using this technique (see ref. [13] http://www.astro.wisc.edu).

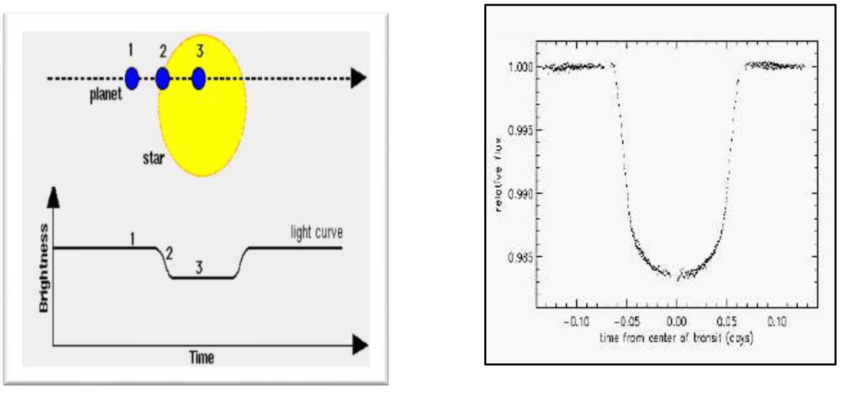


Figure (1): Left: The principles of the transit photometry approach

(see ref. [13] http://www.astro.wisc.edu). Right: light curve showing a transit of star HD209458b by its planet (Uljan, 2015).

2. Gravitational micro-lensing

Gravitational lensing is based on the physical phenomenon that light trajectories are bent in gravitational field. Light from the source star ’S’ is bent by the lens star ’L’, so that the observer ’O’ sees the image ’I’ instead of the true source (figure 2). The micro-lensing technique has many advantages. It is more sensitive than other techniques to detect small-mass planets. It is most sensitive to planets in our Galaxy with orbit sizes of a few astronomical units (like those of Mars or Jupiter) (Uljan, 2015).

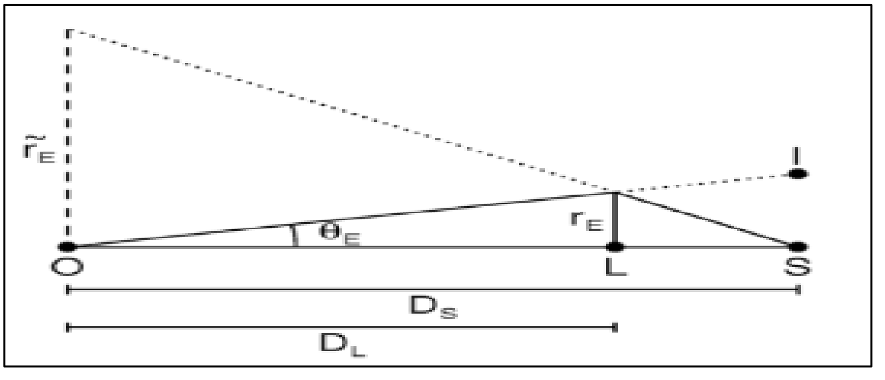


Figure (2): Basic geometry of micro-lensing (Uljan, 2015).

It relies on an effect predicted by Einstein’s General Theory of Relativity: that light rays can be bent by a sufficiently-strong gravitational field. When a planet is orbiting the lensing star, its own gravitational field can contribute to the bending of light rays, and it behaves like a defect in the lens. This defect will produce a narrow spike in the brightness of the lensed star, which can be used to infer the presence of the planet (see ref. [13] http://www.astro.wisc.edu).

If the source star is positioned not just close to the intermediary star when seen from Earth, but precisely behind it, this effect is multiplied (Fig. 3). Light rays from the source star pass on all sides of the intermediary, or "lensing" star, creating what is known as an "Einstein ring" .Even the most powerful Earth-bound telescope cannot resolve the separate images of the source star and the lensing star between them, seeing instead a single giant disk of light, known as the "Einstein disk," where a star had previously been. If a planet is positioned close enough to the lensing star so that it crosses one of the two light streams emanating from the source star, the planet's own gravity bends the light stream and temporarily produces a third image of the source star. When measured from Earth, this effect appears as a temporary spike of brightness Furthermore, the precise characteristics of the micro-lensing light-curve, its intensity and length, tell scientists a great deal about the planet itself. Its total mass, its orbit, and its period can all be deduced with a high degree of accuracy (see ref. [11] http://www.planetary.org).

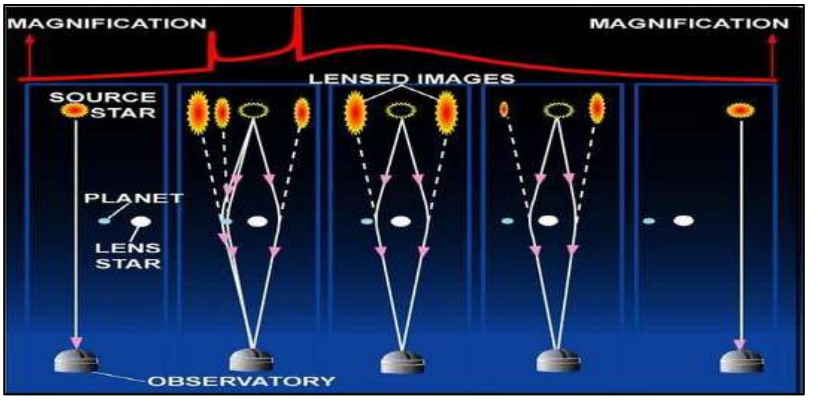


Figure (3): Micro-lensing can reveal exo-planets (see ref. [11] http://www.planetary.org).

3. Pulsar Timing

Pulsar Timing is the method that was used in 1992 by Aleksander Wolszczan and Dale Frail to detect the first confirmed exo-planets (see ref. [12] https://lco.global/spacebook/). A pulsar is a rapidly spinning neutron star with a strong magnetic field. When a planet is introduced, the mutual gravitational pull between it and the pulsar means that they both orbit about their common center of mass (Fig. 4). For two equal-mass objects, the center of mass lies exactly halfway between them; in other situations, the center of mass lies closer to the more-massive object. In the case of a pulsar and a planet, the center of mass will lie very close to the pulsar, since it is much heavier than the planet. Therefore, during one orbit the pulsar will move a much lesser distance than the planet. When the pulsar is moving away from the Earth, the time between each pulse becomes slightly longer; conversely, when the pulsar is moving toward the Earth, the time between pulses becomes slightly shorter (see ref. [13] http://www.astro.wisc.edu).

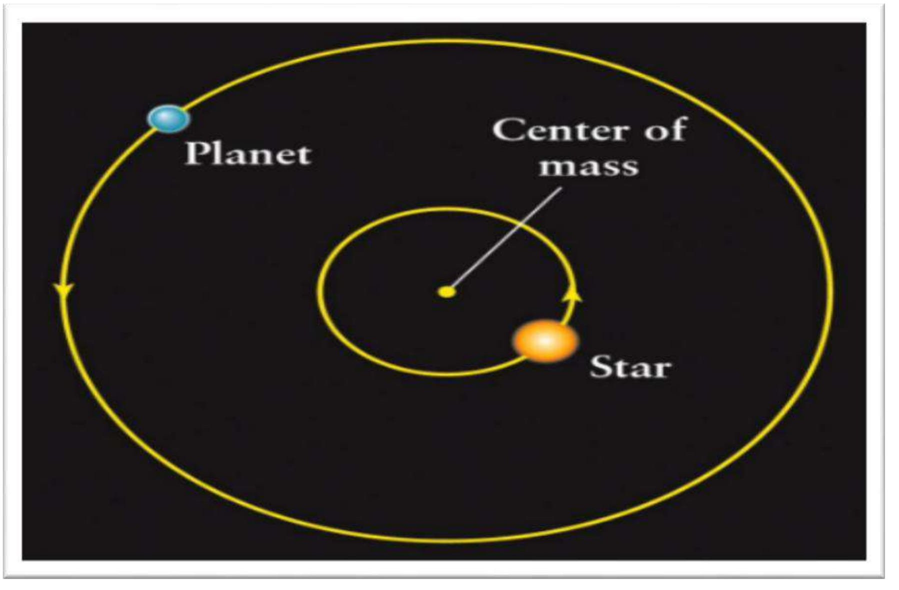


Figure (4) : Shows a star and planet orbiting around their common center of mass (see ref. [13] http://www.astro.wisc.edu).

4. Doppler spectroscopy

The Doppler technique is a good method for discovering exo-planets. It uses the Doppler effect to analyze the motion and properties of the star and planet. The Doppler effect refers to the apparent shift in the wavelength (and frequency) of a wave when there is relative motion between the source of the wave and an observer. The observation of a Doppler shift of the spectral lines of a star indicates a change in the velocity of the star with respect to the observer. When the star moves toward us, the light emitted has a shorter wavelength, so we say its spectrum is blue shifted. When it is moving away from us, the light has a longer wavelength, so we say its spectrum is red shifted (see ref. [9] http://lasp.colorado.edu).

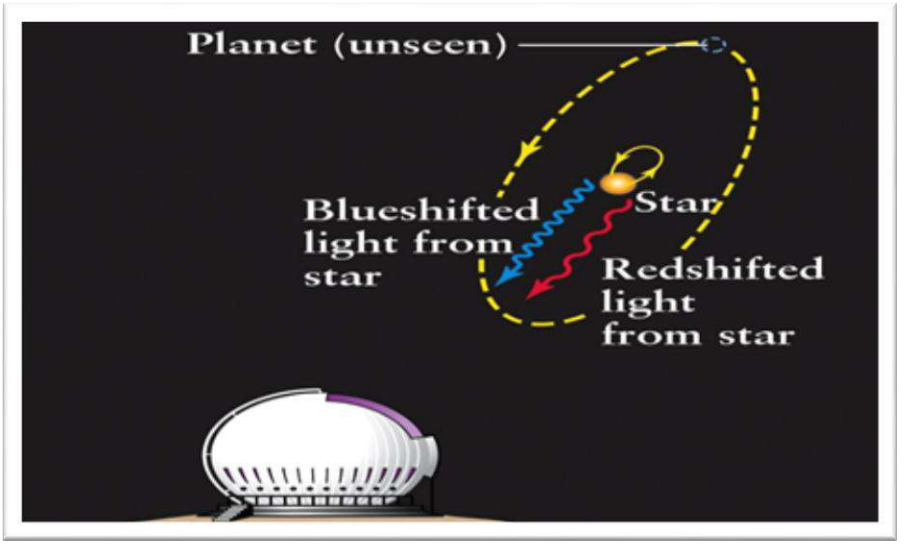


Figure (5) : Shows Doppler shifting (see ref. [13] http://www.astro.wisc.edu).

The radial velocities can be calculated with the aid of the techniques of spectrography and the Doppler effect (Unsoeld et al, 2005):

$$V_r = c\ \frac{\Delta\lambda}{\lambda_0} = \frac{\lambda - \lambda_0}{\lambda_0}$$

Where:

V_r : The radial velocity

c : The speed of light

$\Delta\lambda$: The wavelength shift of light

λ_0: The wavelength of light

The sign radial velocity is defined: $+V_r$ blue shift and $-V_r$ red shift.

A graph of measured radial velocity versus time will give a characteristic curve (sine curve in the case of a circular orbit) and the amplitude of the curve will allow the minimum mass of the planet to be calculated using the binary mass function. The planet's mass is given by (see ref. [10] https:// lasp.colorado.edu):

$$M_{Planet} = \frac{M_{Star} v_{Star} P_{Planet}}{2\pi a_{Planet}}$$

Figure (6) shows an example of one of the lowest amplitude exo-planets, detected with HARPS. The orbital period for this planet is 58.43 days. The data was comprised of 185 observations spanning 7.5 years (Debra, et al., 2014).

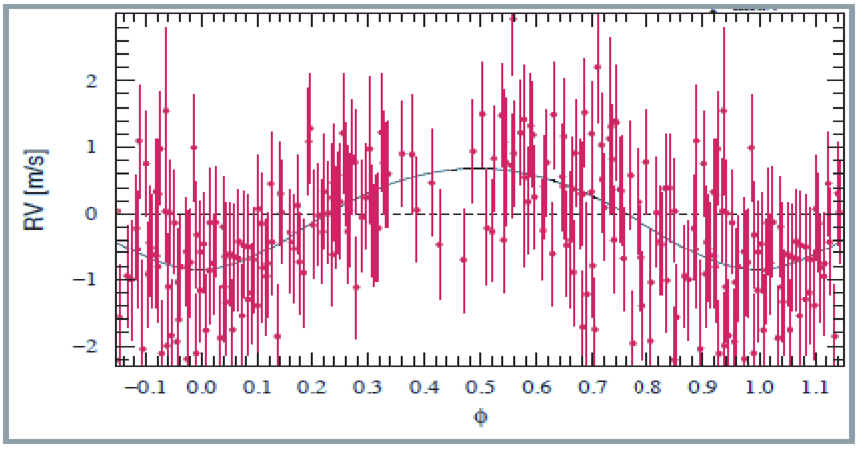


Figure (6) : Shows one of the lowest amplitude exoplanets (Debra, et al., 2014).

Conclusion

Extra-solar planets or exo-planets are planets orbiting stars other than the Sun. Extra-solar planets are incredibly difficult to obtain as the distance of these planets are very much farther from the earth. Hence the indirect techniques were used. All of these methods rely on the fact that a planet exerts a small influence on its parent star as it travels around its orbit. The first confirmation of an exo-planet orbiting a main-sequence star was made in 1995, by Meyor & Queloz, when a giant planet was found in a four-day orbit around the nearby star 51 Pegasi. The discovery was with Doppler spectroscopy method (radial velocities methods).

Beginning with the detection of a planet around the star 51 Pegasi, the Doppler spectroscopy technique has been the most successful so far in finding extra-solar planets, it is best suited to look for very massive planets orbiting close to their parent star.

References

[1]. Debra A. Fischer, Andrew W. Howard, Greg P. Laughlin, Bruce Macintosh, Suvrath M., Johannes Sahlmann, Jennifer C. Yee, Exoplanet Detection Techniques, University of Arizona Press Tucson, 914 pp., p.715-737, (2014).

[2]. Glaser, J. P, 2015, On the Detection of Exoplanets via Radial Velocity Doppler Spectroscopy, Cleveland State University.

[3]. Hans-Jörg D., 1998, Photometric Detection of extrasolar Planets by the Transit Method, On the adress: http://adsbit.harvard.edu//full/1998ASPC..134..216D/0000216.000.html

[4]. Lunine, J. I., Macintosh, B. and Peale, S., 2009, The detection and characterization of exoplanets, Physics Today, May 2009,(page 46-51).

[5]. Uljan, M., 2015, Methods for exoplanet search, University of Ljubljana. Faculty of Mathematics and Physik.

[6]. Unsoeld, A. & Baschek, B., Der neue Kosmos 7. Auflage, Springer-Verlag Berlin Heidelberg New York (2005).

[7]. Wolszczan A. and Frail D. A., 1992, A planetary system around the millisecond pulsar PSR B1257 +12 Nature 355, 145 –147

[8]. A beginners guide to exo-planets, on the address :

http://www.physics.org/article-questions.asp?id=57

[9]. Extrasolar planets, on the address :

http://lasp.colorado.edu/education/outerplanets/exoplanets.php

[10]. Finding masses of extra-solar planets**,** on the address :

https://lasp.colorado.edu/education/outerplanets/math/extrasolar_masses.pdf

[11]. Micro-lensing, on the address :

http://www.planetary.org/explore/space-topics/exoplanets/microlensing .html

[12]. Space Book, 2017, on the address :

https://lco.global/spacebook/pulsar-timing-method/

[13]. The Search for Extra-solar Planets, On the address:

http://www.astro.wisc.edu/~townsend/static.php?ref=diploma-2

Activity coefficient Correlations and Uses.

Melod M. Unis[1], Mohamed M. Alghiryani [2].

1,2- Higher Institute of Sciences And Technology, Gharyan. Libya.

الخلاصة :

يتطلب تصميم المعدات الصناعية بيانات توازن الطور لربط مراحل بخار السائل بدقة متناهية. معاملات التلاشي ومعامل النشاط هي العوامل المستخدمة في الصناعات البتروكيماوية للحد من الانحرافات عن السلوك المثالي في مزيج من المواد الكيميائية. في مزيج مثالي، تكون التفاعلات المجهرية بين كل زوج من الأنواع الكيميائية هي نفسها، وترتبط بالديناميكا الحرارية من خلال علاقات معقدة المرتبطة بالانتروبيا (القصور الحراري) وارتباطات طاقة جيبس الحرة.

ونتيجة لذلك، يمكن التعبير عن خصائص المخاليط مباشرة من حيث التركيزات البسيطة أو الضغوط الجزئية للمواد الموجودة على سبيل المثال. قانون راؤول. يتم استيعاب الانحرافات عن المثالية (الحالة المثالية) عن طريق تعديل التركيز من خلال معامل النشاط. تقدم ورقة المراجعة هذه، مقارنة بين الاساليب الرائدة التي تتناول تقدير معاملات النشاط في المطبوعات (المؤلفات).

يتفاوت الانحراف من مركبات متنوعة إلى أخرى بناءً على التركيب الجزيئي للمركبات والمكونات الجزيئية. حسابات توازن طور البخار السائل هي متطلبات أساسية في التصميم الصناعي. كما تلعب حسابات معامل النشاط ومعامل التلاشي دورًا مهمًا في الحسابات الديناميكية الحرارية.

Abstract:

Design of industrial equipment requires phase equilibrium data to correlate liquid vapor phases with accurate precision. Fugacity coefficients and activity coefficient are factors used in petrochemical industries to minimize the deviations from ideal behavior in a mixture of chemical substances. In an ideal mixture, the microscopic interactions between each pair of chemical species are the same and, are correlated thermodynamically through complex relations associated with entropy and Gibbs free energy correlations. As a result, properties of the mixtures can be expressed directly in terms of simple concentrations or partial pressures of the substances present e.g. Raoult's law. Deviations from ideality are accommodated by modifying the concentration by an activity

coefficient. This review paper present a comparison between leading methods dealing with estimation of activity coefficients in literature. Deviation varies from different structure to another based on molecular structure of the compounds and molecular constituents. Liquid vapor phase equilibria calculations are essential requirements in industrial design. The calculations of activity coefficient and fugacity coefficient play an important role in thermodynamic calculations.

Introduction:

The liquid phase activity coefficient, γ_i, is a function of pressure, temperature and liquid composition. At conditions remote from the critical conditions it is virtually independent of pressure and, in the range of temperature normally encountered in distillation, can be taken as independent of temperature.

Correlations for liquid phase activity coefficients:

Several equations have been developed to represent the dependence of activity coefficients on liquid composition.[1,2,3,4]

1. Margules activity equation:

The Margules activity model is a simple thermodynamic model for the excess Gibbs free energy of a liquid mixture introduced in 1895 by Max Margules.

In chemical engineering the Margules Gibbs free energy model for liquid mixtures is better known as the Margules activity or activity coefficient model.

Margules expressed the excess Gibbs free energy of a binary liquid mixture as a power series of the mole fractions xi:

$$\frac{G^{ex}}{RT} = X_1X_2(A_{21}X_1 + A_{12}X_2) + X_1^2X_2^2(B_{21}X_1 + B_{12}X_2) + \ldots + X_1^mX_2^m(M_{21}X_1 + M_{12}X_2)$$

A, B are constants, which are derived from regressing experimental phase equilibria data.

- **One-parameter margules equation :**

The simplest expression for Gibbs excess energy function:

$$\frac{G^E}{RT} = A x_1 x_2$$

Parameter A is a constant which is not associated with the other uses of the variable (equation of state parameters, Helmholtz energy, Antoine coefficients).

Derive the expressions for the activity coefficients from this expression.

$$\frac{G^E}{RT} = A n_2 \frac{n_1}{n}$$

$$\frac{1}{RT}\left(\frac{\partial G^E}{\partial n_i}\right)_{T,P,n_{j\neq i}} = A n_2\left[\frac{1}{n} - \frac{n_1}{n^2}\right] = A\frac{n_2}{n}\left[1 - \frac{n_1}{n}\right] = A x_2(1 - x_1)$$

$$\ln \gamma_1 = A x_2^2 \qquad \ln \gamma_2 = A x_1^2$$

- **Two-parameters margules equation:**

$$\ln \gamma_1 = x_2^2\left[A_{12} + 2(A_{21} - A_{12})x_1\right]$$

$$\ln \gamma_2 = x_1^2\left[A_{21} + 2(A_{12} - A_{21})x_2\right]$$

2. Van Laar's Equation:

Originally the van Laar(1910) development was based on the van der Waals EOS but since the fit of activity coefficient data with van der

Waals parameters is poor, the van Laar equation now is regarded as a purely empirical one.

Expressions for the activity coefficients,

$$\ln\gamma_1 = \frac{A_{12}}{\left[1+\dfrac{A_{12}x_1}{A_{21}x_2}\right]^2}; \qquad \ln\gamma_2 = \frac{A_{21}}{\left[1+\dfrac{A_{21}x_2}{A_{12}x_1}\right]^2}$$

The point of van Laar theory is to use experimental data for mixtures to estimate the values of A_{12} and A_{21}. These equations can be rearranged to obtain A_{12} and A_{21} from γ_1 and γ_2 given any one VLE point.

$$A_{12} = \ln\gamma_1\left[1+\frac{x_2\ln\gamma_2}{x_1\ln\gamma_1}\right]^2 \qquad A_{21} = \ln\gamma_2\left[1+\frac{x_1\ln\gamma_1}{x_2\ln\gamma_2}\right]^2$$

3. Regular Solution (RS) Model :

This activity coefficient model is derived for solutions that show moderate deviations from ideal solution behavior, and for which V^E and S^E are both zero. The model was proposed by Scatchard and Hildebrand (J. H. Hildebrand & R. L Scott. The Solubility of Non-electrolytes, Dover, 1964) and constitutes one of few models that are derived from theory. Known as the Regular Solution Model, the molar excess Gibbs free energy function is given by:

$$G^E/RT = (x_1V_1 + x_2V_2)\Phi_1\Phi_2(\delta_1-\delta_2)^2$$

$$\ln\gamma_1 = V_1\Phi_2^2(\delta_1-\delta_2)^2$$

$$\ln\gamma_2 = V_2\Phi_1^2(\delta_1-\delta_2)^2$$

where, Φ_i = volume fraction $=\frac{x_iV_i}{V_m}$; V_i = molar volume of pure i^th^ species, and $V_m = \sum_i x_iV_i$

Further: δ_i = solubility parameter for i^{th} species, which is given by:

$$\delta_i = \sqrt{\frac{\left(\Delta U_i^{vap}\right)}{V_i}} \cong \sqrt{\frac{\left(\Delta H_i^{vap} - RT\right)}{V_i}}$$

Where $\Delta U_i^{vap}, \Delta H_i^{vap}$ are molar internal energy, and enthalpy of vaporization of i^{th} species at the temperature of interest.

The above relations may be extended to multi-component mixtures for which**:**

$$RT \ln \gamma_i = V_i \left(\delta_i - \bar{\delta}\right)^2$$

$$\bar{\delta} = \sum_j \Phi_j \delta_j$$

$$\Phi_j = \frac{x_j V_j}{\sum_j x_j V_j}$$

(where, j R runs over all the species) .

4. Free volume and Flory-Huggins Theory:

The volume occupied by one molecule is not accessible to the other molecules. When we mix two components, each component's entropy increases according to how much more space it has:

$$\Delta S_i = N_i\, k \ln(V_{f_m} / V_{f_i})$$

Where V_{fm} = the free volume of the mixture.
V_{fi} = the free volume in the ith pure component.
It is customary to assume that the fraction of free volume in any component is th e same.

$$V_{f_i} = N_i v_i\, v_f$$

Where vi = volume of the i species.

vf = universal fraction of free volume.

The entropy may be taken as that of a perfect gas composed of the same number of molecules confined to a volume equal to the free volume.

$$\frac{\Delta S}{Nk} = x_1 \ln(\frac{V_{f_m}}{V_{f_1}}) + x_1 \ln(\frac{V_{f_m}}{V_{f_2}})$$

$$\frac{\Delta S}{Nk} = x_1 \ln(\frac{n_1 v_1 + n_2 v_2}{n_1 v_1}) + x_2 \ln(\frac{n_1 v_1 + n_2 v_2}{n_2 v_2}) = -\sum x_i \ln \Phi_i$$

$$\frac{\Delta S^E}{Nk} = -\sum x_i \ln \Phi_i + \sum x_i \ln x_i = -\sum x_i \ln(\Phi_i / x_i)$$

For a binary solution,

$$\frac{\Delta G^E}{NkT} = \frac{H^E}{NkT} - \frac{\Delta S^E}{Nk} = x_1 \ln\frac{\Phi_1}{x_1} + x_2 \ln\frac{\Phi_2}{x_2} + \Phi_1\Phi_2 \frac{(\delta_1 - \delta_2)^2}{RT}(x_1 v_1 + x_2 v_2)$$

$$\ln \gamma_1 = \ln(\Phi_1 / x_1) + (1 - \Phi_1 / x_1) + \frac{v_1}{RT}\Phi_2^2(\delta_1 - \delta_2)^2$$

$$\ln \gamma_2 = \ln(\Phi_2 / x_2) + (1 - \Phi_2 / x_2) + \frac{v_2}{RT}\Phi_1^2(\delta_1 - \delta_2)^2$$

5. Wilson equation:

The equation developed by Wilson (1964) is convenient to use in process design:

$$\ln \gamma_k = 1.0 - \ln\left[\sum_{j=1}^{n}(x_j A_{kj})\right] - \sum_{i=1}^{n}\left[\frac{x_i A_{ik}}{\sum_{j=1}^{n}(x_j A_{ij})}\right]$$

Where γ_k = activity coefficient for component k,

Aij, Aji = Wilson coefficients (A values) for the binary pair i, j,

n = number of components.

The Wilson equation is for systems that are severely non-ideal; but, like other equations, it cannot be used to represent systems that form two phases in the concentration range of interest.

A significant advantage of the Wilson equation is that it can be used to calculate the equilibrium compositions for multicomponent systems using only the Wilson coefficients obtained for the binary pairs that comprise the multicomponent mixture. The Wilson coefficients for several hundred binary systems are given in the DECHEMA vapor-liquid data collection, DECHEMA (1977), and by Hirata (1975). Hirata gives methods for calculating the Wilson coefficients from vapor liquid equilibrium experimental data.

6. Non-random two liquid equation (NRTL) equation:

The NRTL equation developed by Renon and Prausnitz overcomes the disadvantage of the Wilson equation in that it is applicable to immiscible systems. It can be used to predict phase compositions for vapor-liquid and liquid-liquid systems.

$$\frac{G^E}{x_1 x_2 RT} = \frac{G_{21}\tau_{21}}{x_1 + x_2 G_{21}} + \frac{G_{12}\tau_{12}}{x_2 + x_1 G_{12}}$$

$$\ln \gamma_1 = x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1 + x_2 G_{21}}\right)^2 + \frac{G_{12}\tau_{12}}{(x_2 + x_1 G_{12})^2}\right]$$

$$\ln \gamma_2 = x_1^2\left[\tau_{12}\left(\frac{G_{12}}{x_2 + x_1 G_{12}}\right)^2 + \frac{G_{21}\tau_{21}}{(x_1 + x_2 G_{21})^2}\right]$$

$$G_{12} = \exp(-\alpha\tau_{12}) \qquad G_{21} = \exp(-\alpha\tau_{21})$$

$$\tau_{12} = \frac{b_{12}}{RT} \qquad \tau_{21} = \frac{b_{21}}{RT}$$

α, b_{12}, and b_{21} are parameters specific to a particular pair of species, and are independent of composition and temperature.

7. Universal quasi-chemical (UNIQUAC) equation:

The UNIQUAC equation developed by Abrams and Prausnitz (1975) is usually preferred to the NRTL equation in the computer aided design of separation processes. It is suitable for miscible and immiscible systems, and so can be used for vapor-liquid and liquid-liquid systems. As with the Wilson and NRTL equations, the equilibrium compositions for a multicomponent mixture can be predicted from experimental data for the binary pairs that comprise the mixture. Also, in the absence of experimental data for the binary pairs, the coefficients for use in the UNIQUAC equation can be predicted by a group contribution method: UNIFAC.

The best source of data for the UNIQUAC constants for binary pairs is the ECHEMA vapor-liquid and liquid-liquid data collection, DECHEMA (1977).

For multicomponent solution:

$$\frac{G^E}{RT}=\sum_j x_j \ln(\Phi_j/x_j)-5\sum_j q_j x_j \ln(\Phi_j/\theta_j)-\sum_j q_j x_j \ln\left(\sum_i \theta_i \tau_{ij}\right)$$

$$\ln\gamma_k=\ln\gamma_k^{COMB}+\ln\gamma_k^{RES}$$

$$\ln\gamma_k^{COMB}=\ln(\Phi_k/x_k)+(1-\Phi_k/x_k)-5\mathrm{q}_k[\ln(\Phi_k/\theta_k)+(1-\Phi_k/\theta_k)]$$

$$\ln\gamma_k^{RES}=q_k\left[1-\ln\left(\sum_i \theta_i \tau_{ik}\right)-\sum_j \frac{\theta_j \tau_{kj}}{\sum_i \theta_i \tau_{ij}}\right]$$

UNIQUAC equation requires two adjustable parameters characterized from experimental data for each binary system.

$$\ln \gamma_1 = \ln(\frac{\Phi_1}{x_1}) + (1 - \frac{\Phi_1}{x_1}) - 5q_1[\ln(\frac{\Phi_1}{\theta_1}) + (1 - \frac{\Phi_1}{\theta_1})]$$
$$+ q_1\left[1 - \ln(\theta_1 + \theta_2 \tau_{21}) - \frac{\theta_1}{\theta_1 + \theta_2 \tau_{21}} - \theta_2 \frac{\tau_{12}}{\theta_1 \tau_{12} + \theta_2}\right]$$

$$\ln \gamma_2 = \ln(\frac{\Phi_2}{x_2}) + (1 - \frac{\Phi_2}{x_2}) - 5q_2[\ln(\frac{\Phi_2}{\theta_2}) + (1 - \frac{\Phi_2}{\theta_2})]$$
$$+ q_2\left[1 - \ln(\theta_1 \tau_{12} + \theta_2) - \frac{\theta_1 \tau_{21}}{\theta_1 + \theta_2 \tau_{21}} - \frac{\theta_2}{\theta_1 \tau_{12} + \theta_2}\right]$$

Where:

$$\Phi_j \equiv \frac{x_j r_j}{\sum_i x_i r_i} \qquad \theta_j \equiv \frac{x_j q_j}{\sum_i x_i q_i}$$
$$r_j = \sum_k v_k^{(j)} R_k; \qquad q_j = \sum_k v_k^{(j)} Q_k$$

R_k parameter => group volume.

Q_k parameter => group surface area.

Molecule size (r_j) and molecule shape (q_j) may be calculated by multiplying the group parameters by the number of times each group appears in the molecule, and summing all the groups in the molecule.

$v_k^{(j)}$ is the number of groups of the k type in the j molecule.

8. Modified separation of cohesive energy density model(MOSCED):

It is Thermodynamic model for the estimation of limiting activity coefficients (also known as activity coefficient at infinite dilution).

$$\ln \gamma_2^{\infty} = \frac{\nu_2}{RT}\left[(\lambda_1 - \lambda_2)^2 + \frac{q_1^2 q_2^2 (\tau_1^T - \tau_2^T)^2}{\psi_1} + \frac{(\alpha_1^T - \alpha_2^T)(\beta_1^T - \beta_2^T)}{\xi_1}\right] + d_{12}$$
$$d_{12} = \ln\left(\frac{\nu_2}{\nu_1}\right)^{aa} + 1 + \left(\frac{\nu_2}{\nu_1}\right)^{aa}$$

$$aa = 0.953 - 0.002314\left(\left(\tau_2^T\right)^2 + \alpha_2^T\beta_2^T\right)$$

$$\alpha^T = \alpha\left(\frac{293K}{T}\right)^{0.8}, \beta^T = \beta\left(\frac{293K}{T}\right)^{0.8}, \tau^T = \tau\left(\frac{293K}{T}\right)^{0.4}$$

$$\psi_1 = POL + 0.002629\alpha_1^T\beta_1^T$$

$$\xi_1 = 0.68\,(POL - 1) + \left[3.4 - 2.4\exp\left(-0.002687(\alpha_1\beta_1)^{1.5}\right)\right]^{(293K/T)^2}$$

$$POL = q_1^4\left[1.15 - 1.15\exp\left(-0.002337\left(\tau_1^T\right)^3\right)\right] + 1$$

Where :

ν	Molar liquid volume
λ	Dispersion parameter
q	Induction parameter
τ	Polarity parameter
α	Hydrogen-bond acidity parameter
β	Hydrogen-bond basicity parameter
ξ and *ψ*	Asymmetry factors
d_{12}	Combinatorial term (modified Flory-Huggins(
Index 1	Solvent
Index 2	Solute

The activity coefficient of the solute and solvent can be extended to other concentrations by applying the principle of the Margules equation. This gives:

$$\ln\gamma_2 = \left(\ln\gamma_2^\infty + 2\left(\ln\gamma_1^\infty - \ln\gamma_2^\infty\right)\Phi_2\right)\Phi_1^2$$
$$\ln\gamma_1 = \left(\ln\gamma_1^\infty + 2\left(\ln\gamma_2^\infty - \ln\gamma_1^\infty\right)\Phi_1\right)\Phi_2^2$$

where

$$\Phi_i = \frac{x_i\nu_i}{\sum_j \nu_j x_j}$$

9. Debye–Hückel equation:

The Debye–Hückel limiting law enables one to determine the activity coefficient of an ion in a dilute solution of known ionic strength.

$$\ln(\gamma_i) = -\frac{z_i^2 q^2 \kappa}{8\pi\varepsilon_r\varepsilon_0 k_B T} = -\frac{z_i^2 q^3 N_A^{1/2}}{4\pi(\varepsilon_r\varepsilon_0 k_B T)^{3/2}}\sqrt{\frac{I}{2}} = -Az_i^2\sqrt{I}$$

z_i is the charge number of ion species i

q is the elementary charge

κ is the inverse of the Debye screening length,

ε_r is the relative permittivity of the solvent

ε_0 is the permittivity of free space

k_B is Boltzmann's constant

T is the temperature of the solution

N_A is Avogadro's number

I is the ionic strength of the solution,

A is a constant that depends on temperature.

Extensions of the theory ;

Extended Debye–Hückel equation is given by:

$$-\log_{10}(\gamma) = \frac{A|z_+ z_-|\sqrt{I}}{1 + Ba\sqrt{I}}$$

The Debye–Hückel equation cannot be used in the solutions of surfactants where the presence of micelles influences on the electrochemical properties of the system.

- **Relation between the model parameters and infinite dilute activity coefficients :**

A common feature of all the models are that the parameters are basically related to the infinite dilute activity coefficients for each binary.[5] Table (1) shows the relation between the model parameters and infinite dilute activity coefficients.

Table (1) shows the relation between the model parameters and infinite dilute activity coefficients.

Model	Relation between the model parameters and infinite dilute activity coefficients
Two-suffix Margules	$\ln \gamma_1^\infty = \ln \gamma_2^\infty = A$
Three-suffix Margules	$\ln \gamma_1^\infty = A_{12}$; $\ln \gamma_2^\infty = A_{21}$
Van Laar	$\ln \gamma_1^\infty = A_{12}$; $\ln \gamma_2^\infty = A_{21}$
Wilson	$\ln \gamma_1^\infty = 1 - \Lambda_{21} - \ln \Lambda_{12}$; $\ln \gamma_2^\infty = 1 - \Lambda_{12} - \ln \Lambda_{21}$
NRTL	$\ln \gamma_1^\infty = \tau_{21} + \tau_{12} \exp(-\alpha\tau_{12})$; $\ln \gamma_2^\infty = \tau_{12} + \tau_{21} \exp(-\alpha\tau_{21})$

- **Comparison of Equations.**

The merits of the individual activity-coefficient correlation methods have been cited locally, and a comparison of a sort is in table (2) . Those conclusions may be summarized.

Table (2) Frequencies of best fits of fine activity coefficient correlations of the DECHEMA vapor-liquid equilibrium data collection

Part of Collection	*Number of Data*	*Margules*	*van Laar*	*Wilson*	*NRTL*	*UNIQUAC*
1 Aqueous organics	504	0.143	0.071	0.240	0.403*	0.143
2A Alcohols	574	0.166	0.085	0.395*	0.223	0.131
2B Alcohols and phenols	480	0.213	0.119	0.342*	0.225	0.102
3/4 Alcohols, ketones, ethers	490	0.280*	0.167	0.243	0.155	0.155
6A C_4-C_6 hydrocarbons	587	0.172	0.133	0.365*	0.232	0.099
6B C_7-C_{18} hydrocarbons	435	0.225	0.170	0.260*	0.209	0.136
7 Aromatics	493	0.260*	0.187	0.225	0.160	0.172
Total of 7 parts	3563	0.206	0.131	0.300*	0.230	0.133

*Identifies the most frequent best fit in each category.

1. The Margules, van Laar, and related algebraic forms have the merit of mathematical simplicity, ease of evaluation of the parameters from activity-coefficient data, and often adequate representation of even fairly non-ideal binary mixtures, including partially miscible liquid systems. They are not applicable to multicomponent systems without ternary or higher interaction parameters.
2. The Wilson equation represents vapor-liquid equilibria of binary and multicomponent mixtures very well with only binary parameters. Because of its greater simplicity it may be preferable to the NRTL and UNIQUAC equations for this purpose. Although it is not directly applicable to liquid-liquid equilibria.
3. The NRTL equation represents vapor-liquid and liquid-liquid equilibria of binary and multicomponent systems quite well, and is often superior to the others for aqueous systems. It is simpler in form than the UNIQUAC method but has the disadvantage of involving three parameters for each pair of constituents. The third parameter α_{12} often can be estimated from the chemical natures of the components, and a strong claim has been made for a universal value α_{12} = -1. The value α_{12} = 0.2 has been adopted for all mixtures in the DECHEMA LLE Data Collection.
4. Although it employs only two parameters per pair of components, the UNIQUAC equation is algebraically the most complex one. It utilizes knowledge of molecular surfaces and volumes of the pure components, which can be estimated from structural contributions, and for this reason the method may be particularly applicable to mixtures of widely different molecular sizes. It is applicable to vapor-liquid arid liquid-liquid equilibria of multicomponent mixtures with binary parameters and pure component data only.

Sample page from the DECHEMA Collection.

Sample Page from the DECHEMA Collection of Vapor-Liquid Equilibrium Data (1979, Vol I/3&4 p. 228)

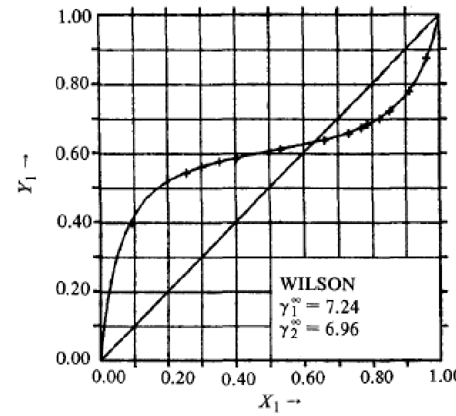
(1) ACETONE	C3H60
(2) HEXANE	C6H14

***** ANTOINE CONSTANTS			REGION *****				CONSISTENCY	
(1)	7.11714	1210.595	229.664	-13-	55 C		METHOD 1	*
(2)	6.91058	1189.640	226.280	-30-	170 C		METHOD 2	*

TEMPERATURE= 20.00 DEGREE C

LIT: RALL W.,SCHAEFER K.,Z.ELECTROCHEM.63,1019(1959).

CONSTANTS:	A12	A21	ALPHA12
MARGULES	1.7448	1.8012	
VAN LAAR	1.7416	1.8044	
WILSON	1077.8013	375.5248	
NRTL	632.4249	583.8331	0.2913
UNIQUAC	−41.9959	512.3937	



EXPERIMENTAL DATA			*MARGULES*		*VAN LAAR*		*WILSON*		*NRTL*		*UNIQUAC*	
P MM HG	*X1*	*Y1*	*DIFF P*	*DIFF Y1*	*DIFF P*	*DIFF Y1*	*DIFF P*	*DIFF Y1*	*DIFF P*	*DIFF Y1*	*DIFF P*	*DIFF Y1*
119.60	0.0	0.0	−0.67	0.0	−0.67	0.0	−0.67	0.0	−0.67	0.0	−0.67	0.0
187.20	0.0913	0.3966	4.24	0.0024	4.35	0.0028	−1.26	−0.0110	2.90	−0.0011	3.60	0.0008
226.70	0.2563	0.5421	−0.19	−0.0166	−0.13	−0.0166	1.52	−0.0023	0.07	−0.0137	−0.01	−0.0151
232.30	0.3019	0.5595	0.85	−0.0161	0.89	−0.0162	3.13	−0.0007	1.28	−0.0128	1.10	−0.0144
232.40	0.3543	0.5737	−2.36	−0.0154	−2.33	−0.0155	−0.02	−0.0009	−1.89	−0.0121	−2.09	−0.0137
237.00	0.4035	0.5827	0.37	−0.0153	0.38	−0.0155	2.40	−0.0032	0.76	−0.0125	0.58	−0.0139
238.80	0.5325	0.6092	−0.02	−0.0043	−0.03	−0.0046	0.92	−0.0020	0.10	−0.0039	0.04	−0.0043
237.70	0.6609	0.6362	−1.47	0.0045	−1.49	0.0042	−0.89	−0.0028	−1.44	0.0027	−1.46	0.0033
239.30	0.7309	0.6564	1.22	0.0065	1.20	0.0063	1.76	−0.0033	1.24	0.0042	1.22	0.0052
237.90	0.7679	0.6722	1.21	0.0081	1.19	0.0080	1.62	−0.0017	1.20	0.0060	1.19	0.0069
234.30	0.7862	0.6825	−1.38	0.0097	−1.41	0.0097	−1.10	0.0004	−1.43	0.0078	−1.43	0.0086
234.10	0.8219	0.6975	1.18	0.0038	1.14	0.0038	1.08	−0.0037	1.02	0.0024	1.07	0.0030
230.30	0.8528	0.7202	0.88	0.0028	0.83	0.0028	0.29	−0.0021	0.60	0.0021	0.70	0.0024
220.60	0.9105	0.7778	1.70	−0.0051	1.64	−0.0049	−0.07	−0.0026	1.18	−0.0041	1.38	−0.0044
202.90	0.9619	0.8739	−0.14	−0.0071	−0.18	−0.0069	−2.24	0.0009	−0.66	−0.0050	−0.44	−0.0059
181.50	1.0000	1.0000	−3.96	0.0	−3.96	0.0	−3.96	0.0	−3.96	0.0	−3.96	0.0
MEAN DEVIATION:			1.23	0.0084	1.23	0.0084	1.31	0.0027	1.13	0.0064	1.17	0.0073
MAX. DEVIATION:			4.24	0.0166	4.35	0.0166	3.13	0.0110	2.90	0.0137	3.60	0.0151

Application of Activity Coefficient Models;

- Activity coefficients are used in phase equilibria calculation for modeling equilibrium properties.[(6),(7)] As shown in the following table.

$$y_i P = x_i \gamma_i P_i^{sat}$$

System Type	Models
Species similar in size and shape	**One-constant Margules**
Moderately non-ideal mixtures	**Two-constant Margules, Van Laar, Regular Solution**
Strongly non-ideal mixtures (for example Alcohols +Hydrocarbons)	**Wilson, NRTL, UNIQUAC**
Solutions with miscibility gap	**NRTL, UNIQUAC**

- **Calculation of solubility :**

Experimental determination of solubility is time consuming and costly, therefore it is effective to use activity coefficient models to predict solubility

In Equilibrium:

$$a^{solid} = a^{solute} = x^{sat} \gamma^{sat}$$

Solubility can be calculated as follow

$$x = \frac{a^{solid}}{\gamma}$$

a^{solid} is activity of solid which is function of physical properties of solid like melting temperature, heat of fusion and heat capacity γ is activity coefficient.

References:

[1] Stanley M. Phase Equilibria in Chemical Engineering, Walas, Butterworth Publ. (1985)

[2] Lazzaroni M. J.; Bush D.; Eckert C. A.; Frank T. C.; Gupta S.; Olson J. D. "Revision of MOSCED Parameters and Extension to Solid Solubility Calculations". Ind. Eng. Chem. Res. 44.(2005).

[3] SMITH, J. M., VAN NESS, H. C., & ABBOTT, M. M. (1996). Introduction to chemical engineering thermodynamics. New York, McGraw-Hill Companies.

[4] King, M B. Phase Equilibrium in Mixtures. Oxford: Pergamon Press, (1969). Internet resource.

[5] MAURER, G., & PRAUSNITZ, J. (1978). On the derivation and extension of the unique equation. Fluid Phase Equilibria. 2, 91-99.

[6] The properties of gases & liquids:4th Edition. Robert C. Reid, John M. Prausnitz, and Bruce E. Poling, McGraw-Hill Book Company.

[7] https://en.wikipedia.org/wiki/Activity_coefficient.

The ICT in North Africa Region: Facts for Sustainable Future

Ahmad R. Kobaiz[1], Seddeq E. Gharare[2], Alsayah Ali Emhemed[3]

[1] Department of Electrical Engineering, the Higher Institute of Science and Technology, Gharyan – Libya.

[2] Department of Electrical and Computer Engineering, Faculty of Engineering, University of Gharyan – Libya.

[3] Department of Electrical Engineering, College of Technical Sciences, Bani Waled – Libya.

المستخلص:

مع تزايد استخدام تكنولوجيا المعلومات والاتصالات ، فإن الابتكار والتطوير في قطاع تكنولوجيا المعلومات والاتصالات يتزايد ويشهدان ثورة في معظم دول العالم. و أصبح دور تكنولوجيا المعلومات والاتصالات مهماً كأدوات يمكن للحكومات نشرها في برامج الحد من الفقر لتسريع النمو الوطني. فمثلا في قارة أفريقيا ، تحقق تنمية تكنولوجيا المعلومات والاتصالات تقدما سريعا في توفير منافع اقتصادية واجتماعية هائلة للقارة ، ولكن الافتقار إلى الجودة والمعلومات المستدامة في عدد من مجالات التنمية لا يزال يمثل قضية حقيقية.

تعرض هذه الدراسة حالة تكنولوجيا المعلومات والاتصالات في الدول الموجودة في المنطقة الشمالية من قارة أفريقيا. تم إجراء دراسة المراجعة باستخدام مؤشر تطوير تكنولوجيا المعلومات والاتصالات (**IDI**). يعد **IDI** أداة قياسية لقياس الأداء ، ويستخدم لرصد ومقارنة التطورات في تكنولوجيا المعلومات والاتصالات عبر البلدان.

تظهر دراسة المراجعة المقارنة التحليلية بين دول منطقة شمال أفريقيا وتشمل تونس والمغرب وليبيا ومصر وموريتانيا والجزائر باستخدام أدوات تكنولوجيا المعلومات والاتصالات **ICT** و **IDI** كأفضل ادوات لمراقبة ورصد أي تحسن في النمو الوطني.

Abstract:

With the growing use of ICT, the innovation and development in the ICT sector is increasing and witnessing a revolution in the most of world countries. The role of ICTs becomes important as tools that governments can deploy in their poverty reduction programs to accelerate the national growth. In the Africa continent, the ICT development is making rapid progress offering huge economic and social benefits for the continent,

but the lack of quality and sustainable information in a number of development areas remains a real issue.

This study presents the state of ICT in the development nations located in the north region of Africa continent. This review study is carried out using the ICT Development Index (IDI). The IDI is a standard tool for benchmarking, and it is used to monitor and compare developments in information and communication technology (ICT) across countries.

The review study shows analytical comparison between the North Africa Region Countries includes Tunisia, Morocco, Libya, Egypt, Mauritania and Algeria using ICT and IDI tools as the best ones to monitor and notice any improvement in national growth.

Keywords: ICT, IDI, Internet, Mobile, Fixed line.

I. Introduction

The ICT stands for Information and Communication Technology and defined as divers set of technological tools and resources used to communicate, produce, disseminate, accumulate, and manage information. These technologies include radio, TV, computers, fixed lines telephones, mobile communications, and Internet. ICT has become a prominent and crucial sector which is widely used in the entire world for many important and different purposes, such as business, health, transport, communication, and education [1]. As a result, the ICT has played a significant role in the economic growth for developed and developing countries in the world. In Africa continent, Information and Communication Technology (ICT) has been making considerable progress since the beginning of the 21st century. The ICT developments can be used as determining factor and instruments for general growth, this factor and instruments, including not only computer hardware and software but also fixed telephones, mobile telephones, telecommunication equipment and wireless transmission equipment.

Currently, total worldwide mobile subscription have grown to 7 billion and mobile internet subscription to 3 billion at the end of 2014, and these numbers are expected to double within five years. The increase is mostly due to growth in the developing world [2]

Timely and comparable data remains a major barrier to analyzing the status and progress of Information and communication technologies, identifying reliable targets and adapting policies.

This paper presents a study about the Arab countries which are located in the north of Africa continent in terms of the usage of the ICT. The purpose of this paper is to identify and present opportunities for ICTs development, and determine a collaborative framework for ICTs for North African countries, premised on the developmental indices for establishing an information and knowledge society

Also, this study is carried out using the ICT Development Index (IDI). The ICT Development Index (IDI) is a composite index combining some indicators into one benchmark measure that serves to monitor and compare developments in information and communication technology (ICT) across countries [2].

II. Literature Review

Africa is the world's second-largest and second-most-populous continent. At about 30.2 million km^2 including adjacent islands, it covers six percent of earth's total surface area and 20.4 percent of its total land area [3]. With 1.1 billion people as of 2013, it accounts for about 15% of the world's human population [4]. The continent is surrounded by the Mediterranean Sea to the north, both the Suez Canal and the Red Sea along the Sinai Peninsula to the northeast, the Indian Ocean to the southeast, and the Atlantic Ocean to the west.

Africa is considered as a vast continent with huge contrasts and non-homogeneous development of telecommunications and ICTs. These contrasts are evident even within the sub regions themselves and also within individual countries. It is tempting to simplify the grouping of African Countries into three groups as the relatively well developed Northern African and South Africa, and the least developed sub-Saharan Africa.

Virtually all major indicators e.g. GDP per capita, ICT, human development index, literacy, power consumption, child mortality, life expectancy, …etc easily betray Africa as being at the tail of the other continents. While the continent has 15% of the world population, its share of world GDP is only 1%, while it has 17% of the world phones and barely 1.5% of the global Internet users. One of the most cited statistics is that in 1984 the continent had fewer phones than the city of Tokyo and in 2002 it had less Internet users than London. [5]

In the most countries of the world ICT infrastructure is expanding and modernizing. Recognizing the critical role of information and communication technology in economic development, governments have been pouring large sums into expanding and improving local infrastructures. As a result ,the gap separating the developing and the developed countries has been shrinking in many types of ICT such as number of mobile subscribers, number of fixed telephone lines and Internet users … etc.

According to the Commonwealth of Learning report, which provided a good summary of ICT developments in Africa, The Radio is the most widespread communications medium on the continent. About the Internet connection, 49 of 54 countries and territories in Africa have Internet access in their capital cities [5]. Only 17 countries have Internet servers in their secondary towns, imposing the requirement for long distance calling in order to access the service. The Internet Service Provider (ISP) subscription fee was estimated to an average of US$ 50/month. Each computer in Africa with an Internet connection has an average of three users. The Internet access levels in Africa are one user for every 1400 people compared to a world average of one user for every 35 people and a North American average of one user for every 3-4 people.[6]

In addition to the internet access level, Mobile subscriptions is another indicator of the ICT developments. Mobile subscriptions in the developed world is rapidly reaching saturation point. There are 1.5 billion subscriptions in developed nations, which is similar to 2013. With 120.8 percent mobile penetration, there is already more than one mobile subscription per person in developed nations, leaving little room for growth [2].

In Africa continent, the penetration has grown at 69 per cent by end 2014, which is considered the region with the strongest mobile-cellular growth. The growth trend in Africa is not different. It is expectation that the mobile subscriber base will rise to 100 per cent billion at the end of 2015 [2]. This growth therefore requires more reliable and sustainable infrastructure for effective operation.

To analyze the real use and potential of ICTs, it is imperative that countries carry out representative household and individual ICT surveys. Few African and Arab countries currently do so, though. This adds to the already existing statistical divide on access to, and use of, ICTs [7].

Table 1 presents a simple comparison between four zones of the globe classified as developed countries, developing countries, Africa continent countries and Arab countries.

Table 1 Key Global Telecom Indicators for the World Telecommunication Service Sector in 2014 [2]

Key indications	Developed nations	Developing nations	Africa	Arab States
Mobile cellular subscriptions (millions)	1,515m	5,400m	629m	410m
Per 100 people	120.8%	90.2%	69.3%	109.9%
Fixed telephone lines (millions)	511m	636m	12m	33m
Per 100 people	40.8%	10.6%	1.3%	8.7%
Active mobile broadband subscriptions (millions)	1050m	1265m	172m	92m
Per 100 people	83.7%	21.1%	19.0%	24.0%
Mobile broadband growth	11.5%	26%	43%	19%
Fixed broadband subscriptions (millions)	345m	366m	3m	12m
Per 100 people	27.5%	6.1%	0.4%	3.1%

Table 1 showed that Africa has the lowest growth in all aspects of the ICT compared with the other regions in the world. This indicates that the African ICT environment and infrastructure faces tremendous challenges. Africa is one of the poorest regions in the world and has the lowest access to information and communication resources, which means that there are still challenges for Africa continent in the ICT sector, therefore, the opportunity to invest in the ICT sector and the ICT market in Africa is significant. A number of African countries have made progress on access to ICT services but the continent largely lags behind the rest of the world.

III. Information and Communication Technology Development Index (IDI)

The ICT Development Index (IDI), which has been published annually since 2009, is a composite index that combines 11 indicators into one benchmark measure. It is used to monitor and compare developments in information and communication technology (ICT) between countries and over time [9].

The main objectives of the IDI are [9]:

- To measure the level and evolution over time of ICT developments within countries and the experience of those countries relative to others;
- To measure progress in ICT development in both developed and developing countries;
- To measure the digital divide, i.e. differences between countries in terms of their levels of ICT development; and
- To measure the development potential of ICTs and the extent to which countries can make use of them to enhance growth and development in the context of available capabilities and skills.

The Index is designed to be global and reflect changes taking place in countries at different levels of ICT development. It therefore relies on a limited set of data which can be established with reasonable confidence in countries at all levels of development. Based on this conceptual framework, the IDI is divided into the following three sub-indices:

- Access sub-index: This sub-index captures ICT readiness, and includes five infrastructure and access indicators (fixed-telephone subscriptions, mobile-cellular telephone subscriptions, international Internet bandwidth per Internet user, households with a computer, and households with Internet access).

- Use sub-index: This sub-index captures ICT intensity, and includes three intensity and usage indicators (individuals using the Internet, fixed broadband subscriptions, and mobile-broadband subscriptions).
- Skills sub-index: This sub-index seeks to capture capabilities or skills which are important for ICTs. It includes three proxy indicators (mean years of schooling, gross secondary enrolment, and gross tertiary enrolment). As these are proxy indicators, rather than indicators directly measuring ICT-related skills, the skills sub-index is given less weight in the computation of the IDI than the other two sub-indices.

IV. The IDI Calculation

The above mentioned three Sub-indices were computed by summing the weighted values of the indicators included in the respective subgroup as follows:

- ICT access is measured by fixed-telephone subscriptions per 100 inhabitants, mobile-cellular subscriptions per 100 inhabitants, international Internet bandwidth per Internet user, the percentage of households with Internet computer and the percentage of household's access.

- ICT usage is measured by the percentage of individuals using the Internet, fixed-broadband Internet subscriptions per 100 inhabitants and active mobile-broadband subscriptions per 100 inhabitants.

- ICT skills are approximated by mean years of schooling, secondary gross enrolment ratio and tertiary gross enrolment ratio.

V. The ICT Situation in North Africa

Many analysts of African issues find it quite convenient to group African countries into three groups, the North, South Africa and Sub-Saharan Africa.

North Africa, consisting of the six States, is the most advanced sub-region in telecommunications and ICT development as reflected by its various indicators. It is well connected with submarine cables in the Mediterranean.

The oil and gas wealth in this sub-region has brought overall relatively good socio economic development and peace. Given this situation, these countries hold a potential of extending investments into other countries south of the Sahara to boost ICT development.

The following table 2 [8], is the status of the information and communication technology (ICT) markets in six Arab countries located in North Africa region, including significant infrastructure developments, and government policy and initiatives to improve the access and use of ICTs for households and individuals.

Table 2. ICT in North Africa Countries [8]

Key indications (2017)	Algeria	Egypt	Libya	Morocco	Mauritania	Tunisia	Arab States	World
Fixed telephone sub. Per 100 inhab	8.2	7.1	21.5	6.0	1.3	8.6	7.7	16.6
Mobile cellular sub. Per 100 inhab	113.9	113.7	119.8	120.7	86.5	125.8	107.1	101.5
Fixed – broadband sub. Per 100 inhab	6.9	5.2	2.6	3.7	0.3	5.6	4.7	12.4
Active mobile-broadband sub. Per 100 inhab	64.6	52.6	34.9	46	30.2	63	45.2	52.2
3G coverage (% of population)	83.4	98.7	78.1	95	41	99	81.9	85
LTE/WiMAX coverage (% population)	3.6	0.0	n.a.	68	00	73	33.8	66.5
Mobile –	2.5	0.8	1.3	4.4	16.3	0.9	4.3	5.2

cellular prices (% GNI pc)								
Fixed – broadband prices (%GNI pc)	3.6	1.8	4.4	4	10	1.4	10.1	13.9
Mobile – broadband prices 500MB (% GNI pc)	2.6	0.7	1.5	2	29.2	1.4	4.5	3.7
Mobile – broadband price BB (% GNI pc)	5.4	0.9	2.2	4	29.2	1.1	5.5	6.8
percentage of households with computer	38.4	53.1	23.5	54.9	5.0	39.3	43.3	46.6
Percentage of households with internet access	34.7	43.3	22	68.5	11.2	37.5	45.3	51.5
Percentage of individuals using the internet	42.9	39.2	20.3	58.3	18	49.6	41.8	45.9
Int. internet BW per internet user (k bit/s)	40	17.2	5.5	25.7	4.5	32	39	74.5

The three IDI Sub-indices for the six North African countries which are involved in this study are summarized in the following table:

Table 3: IDI for 6 Arab states in North Africa region [10]

Country	IDI Access sub index	IDI use sub index	IDI skills sub index	IDI 2017 rank	IDI 2017 value
Algeria	5.14	3.38	6.29	102	4.67
Egypt	5.40	3.35	5.66	103	4.63
Libya	4.80	1.98	6.99	115	4.11
Morocco	6.06	3.68	4.35	100	4.77
Mauritania	2.96	1.62	2.15	151	2.26
Tunisia	5.11	4.11	5.67	99	4.82

From the previous table, it can be noticed that Tunisia is ranked as the best country in North Africa Arab states in field of communication and information technology and the lowest is Mauritania for the last year 2017.

VI. Conclusion

Information and communication technologies (ICT's) have the impact effect on the societies around the globe. ICT market in North Africa region will see more innovation. Internet users and Internet penetration rates are low in the most of these countries. Operators will be forced to update their network infrastructure to accommodate increased demand for broadband.

The result of this paper demonstrates that the North Africa countries; Algeria, Egypt, Libya, Morocco, Mauritania and Tunisia are not powerhouses of ICT. ICT skills will remain one of the biggest challenges facing those countries. Moreover, all countries in this region need new ICT policies and need to do more investments in the ICT infrastructure. There are specific interventions that the Africa Continent in general and North Africa countries can develop to sustain and further grow the ICT sector.

Despite critical political situation in Libya (war 2011), it has the highest IDI skills sub index between the 6 countries.

IDI reflects the infrastructure of the country itself accordingly Tunisia is the best between the mentioned 6 Arab countries.

References:

[1] Murray James, 2011. "Cloud network architecture and ICT - Modern Network Architecture". IT Knowledge Exchange. Retrieved 2013-08-18.

[2] Measuring the Information Society Report, 2014 International Telecommunication Union-ITU www.itu.int.

[3] Sayre, April Pulley (1999), *Africa*, Twenty-First Century Books. ISBN 0-7613-1367-2.

[4] World Population Data Sheet. http://www.prb.org/pdf12/2012-population-data-sheet_eng.pdf

[5] International Telecommunication Union, 2003, Assessment of Telecommunication and ICT Infrastructure in Africa, ITU Symposium: Africa ICT Roadmap to Achieve NEPAD Objectives, Arusha ,Tanzania, 1-3 April 2003

[6] Athanase, N. ; Jiang Cangru ; Li Hongbing ; Chen Zhihua, Organizational E-Learning Strategies for Technical and Vocational Education and Training (TVET) in Sub-Sahara Africa, the 2008 IEEE International Conference on Computer Science and Software Engineering, 12 Dec - 14 Dec 2008, Wuhan, China

[7] ICT for Development: Improving Policy coherence, 2010, OECD

[8] https://www.itu.int/en/ITU-D/Statistics/Documents/publications/misr2017/MISR2017_Volume2.pdf

[9] https://www.itu.int/en/ITU-D/Statistics/Pages/publications/mis2017/methodology.aspx

[10] https://www.itu.int/net4/ITU-D/idi/2017/index.html#idi2017rank-tab

