NEURO FUZZY AND HYBRID MODELING OF SUPERCRITICAL FLUID EXTRACTION OF *PIMPINELLA ANISUM L*. SEED

MEYSAM DAVOODY

UNIVERSITI TEKNOLOGI MALAYSIA

NEURO FUZZY AND HYBRID MODELING OF SUPERCRITICAL FLUID EXTRACTION OF *PIMPINELLA ANISUM L*. SEED

MEYSAM DAVOODY

A research submitted in partial fulfillment of the
requirements for the award of the degree of
Master of Engineering (Chemical)

Faculty of Chemical Engineering
Universit Teknologi Malaysia

June 2012

To my beloved mother, Fariba, my lovely wife, Parastoo, and kind parents of my wife, Tahere, and Mehdi. Won't forget your helps, supports, and encourages.

ACKNOWLEDGMENT

This research would not have been possible without the support of many people. I am heartily thankful to my supervisor, Assoc. Prof. Dr. Gholamreza Zahedi, who was abundantly helpful and offered invaluable assistance, support and guidance. I also need to thank greatly my respectful co-supervisor Adjunct. Prof. Dr. Mazda Biglari who offered me limitless help in any case I needed. His valuable comments have had considerable impact on my research. My sincere appreciation also extends to all my friends who have provided assistance at various occasions specially Mr. Abbas Azarpour, Mr. Aqeel Ahmed Bazmi, and Mr. Amjad Riaz who warmly welcomed me several times and provided me with their valuable knowledge and experience. Also I wish to express my love and gratitude to my beloved mother, wife and family of my wife for their support and endless love throughout my studies. Lastly, I offer my regards and blessings to all of those who supported me in any respect during the completion of the research.

ABSTRACT

In the current study, a Neuro-Fuzzy model has been developed to predict the mass of extract in the process of supercritical fluid extraction of *Pimpinella anisum L*. seed. The adaptive-network-based fuzzy inference system (ANFIS) technique was trained with the recorded data from kinetic experiments of the mentioned process at pressures of 8, 10, 14 and 18 MPa and constant temperature of 303.15 K which generated the membership function and rules that excellently expounded the input/output correlations in the process. Excellent prediction with Root Mean Square Error (RMSE) of 0.0235 was observed. In the next step of study, mass transfer coefficient in terms of Sherwood number was estimated by a neuro-fuzzy network. Then, the estimated mass transfer coefficient was introduced into the mathematical model. The proposed gray box (hybrid) model was validated with the experimental data. Results confirmed that equipping mathematical model with neuro-fuzzy network improved performance of the model significantly. Shokri *et al.* (2011) applied Artificial Neural Networks and mathematical modeling on this process, and reported the results of the proposed models. In the last part of this thesis, all four models (including two proposed models of this study) were compared. It was concluded that neuro-fuzzy and gray box models had the best performance.

ABSTRAK

Dalam kajian semasa, model Neuro-Fuzzy telah dibina untuk menjangka jisim yang diekstrak dalam proses pengekstrakkan cecair superkritikal benih *Pimpinella anisum L*. Kaedah sistem inferens berasaskan rangkaian kabur (ANFIS) telah dilatih dengan data yang direkod daripada eksperimen kinetik untuk proses yang dinyatakan pada tekanan 8, 10, 14 dan 18 MPa dan suhu malar 303.15 K yang menjana fungsi keahlian dan peraturan yang berjaya menjelaskan korelasi suapan/keluaran dalam proses tersebut. Jangkaan yang bagus dengan punca purata ralat kuasa dua (RMSE) 0.0235 telah diperhatikan. Dalam langkah seterusnya, pekali jisim yang dipindahkan dalam bentuk nombor Sherwood telah dianggarkan dengan rangkaian neuro-fuzzy. Kemudian, anggaran pekali jisim yang dipindahkan telah diperkenalkan ke dalam model matematik. Model kotak kelabu (hybrid) yang dicadangkan telah disahkan dengan data eksperimen. Keputusan mengesahkan bahawa model matematik yang dilengkapi dengan rangkaian neuro-fuzzy menambah baik persembahan model secara ketara. Shokri *et al.* (2011) menggunakan Rangkaian Neural Buatan dan model matematik pada proses ini, dan melaporkan keputusan untuk model yang dicadangkan. Pada bahagian akhir tesis ini, semua empat model (termasuk dua yang dicadangkan dalam kajian ini) dibandingkan. Disimpulkan bahawa model neuro-fuzzy dan kotak kelabu mempunyai persembahan yang terbaik.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Supercritical fluid extraction (SFE) is a novel and potential separation technique in food science, chemical engineering, and petroleum industry. SFE is effective in solving a number of problems in different areas, such as energy reduction, waste treatment, chemical separation and biotechnology (Kaihara *et al*., 2002; Lucas *et al*., 2002; Oliveira *et al*., 2002; Rozzi *et al*., 2002; Baysal *et al*., 2000). SFE has already proved itself as an attractive technique for selectively removing compounds from food matrices (Shokri *et al.*, 2011). Especially, SFE technique offers the possibility of mild extraction rate conditions combined with low energy requirements for solvent recovery Akinulua *et al*. (2008). In our daily products, SFE has also a worldwide impact. For example, in decaffeinated coffee and tea, the supercritical fluid is used to extract the extra caffeine from the coffee beans and tea leaves; in cholesterol-free butter and egg, the cholesterol is removed by a supercritical fluid (Mezzomo *et al*., 2009).

In recent years, many studies have been focused on SFE techniques to extract pigments, fatty acids, sterols, spices' essential oils, nutrient materials, etc. and a lot of literature is available on SFE from a wide variety of substrates, such as leaf protein concentrates, carrots, algae, sweet potatoes, tomato waste, etc (Reverchon and Poletto, 1996).

A supercritical fluid is the state of substance which can have properties of both liquid and gas at the same time. There are three physical states: solid, liquid, and gas. When a gas is heated above its critical temperature (T_c) or a liquid is compressed above its critical pressure (P_c), supercritical fluids are formed. Generally, when a substance is heated above its critical temperature, regardless of the pressure, the liquid phase cannot exist, but when a substance's temperature and pressure are above its critical temperature and critical (vapor) pressure, called as critical point, such a substance is called a supercritical fluid. At this state, gas and liquid can coexist. A supercritical fluid shows specific properties which are different from properties of gas and liquid states (Clifford, 1998). Figure 1.1 presents the phase diagram of a single substance to illustrate the phase change process.

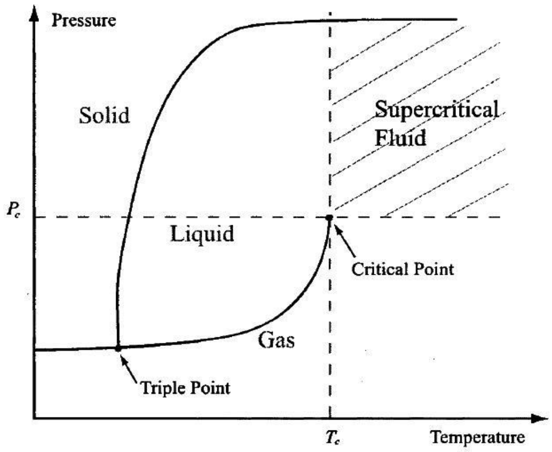

Figure 1.1 The phase diagram for a pure substance (Clifford, 1998)

SFE is the process of separation of a substance using supercritical fluid. Figure 1.2 shows the schematic diagram of a typical extraction process. An extraction fluid, such as carbon dioxide, is first pumped as a cooled liquid and initially cooled to a reservoir.

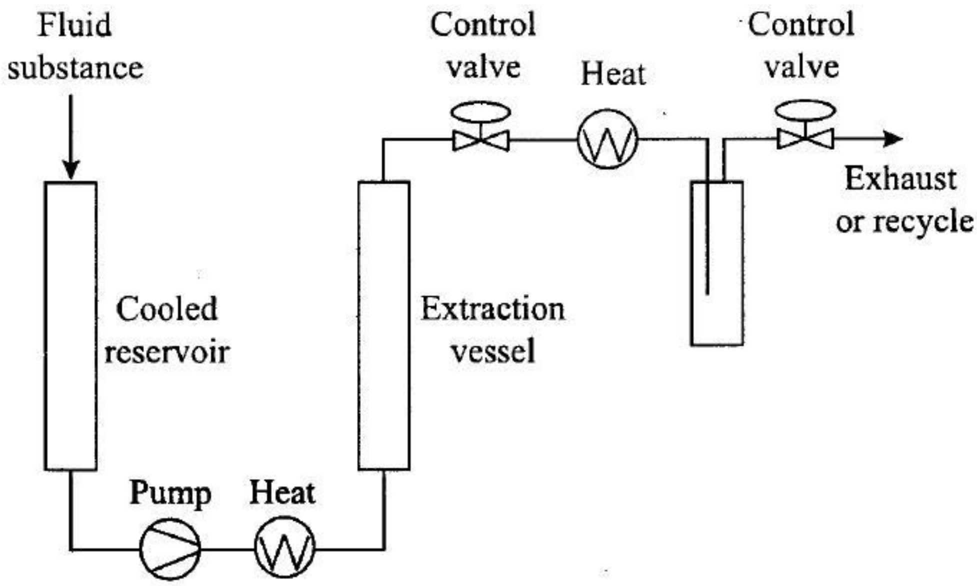

Figure 1.2 Typical SFE diagram (redrawn from Clifford, 1998)

The extraction fluid is then heated to (T_c) and pumped into the extraction vessel, which contains many extraction cells at the same temperature. Here, the material matrix that needs to be extracted is packed into the extraction cell for extraction. After extraction, temperature and pressure are reduced, resulting in the recovery of extracted substance. Then the precipitated material can be collected at a collection vessel. The rate of SFE process depends basically on the rate of mass transfer. Adjusting pressure and temperature can affect solvent density and viscosity. That is, because its density is about of liquids (better solvency) and its viscosity is similar of gases (better penetration), supercritical fluids are significantly more efficient in mass transfer compared with liquid extraction, when operational and material constrains allows (Clifford, 1998).

The main advantages of using supercritical fluids for extractions are (Baysal *et al*., 2000):

i. The extraction process is very rapid.

ii. The solvent for extraction is easy to remove.
iii. The pressure, temperature, and other operational conditions can be used to control the process.
iv. The solvent (such as carbon dioxide and ethane) is relatively cheap.
v. SFE does not cause contamination.
vi. It is less costly to dispose of safely.

Pimpinella anisum L. Umbelliferae is the botanical name of Anise which belongs to the Apiaceae (also known as Umbelliferae) plant family. It is an annual herb indigenous to Iran, India, Turkey and many other warm regions in the world (Zargari, 1989). This plant is a dainty herbaceous plant with white flowers. The main components are Anisaldeheyde, Estragole, Eugenol, Isoeugoenol, γ-himachalene, Anisole, Acetoanisol, (p)-anisic acid, and (e)-Anethole. (E)-Anethole forms the most (75–90%) of the essential oil (Santos *et al.,* 1998). Also fruits, known as aniseed, contain 1–4% of essential oil. Perfumery, medicine, and flavouring industries use essential oil of *Pimpinella anisum L* as feedstock. Medicinal applications include its use as an appetizer, carminative and sedative agent, or for stimulating milk production in breast-feeding mothers (ÖZEL., 2009). In Iranian folk medicine, the plant and especially its fruit essential oil have been used for treatment of some disease including seizures and epilepsy (Avicenna, 1988). The aqueous extract of flowers, stems and leaves of *Pimpinella Anisum. L* has been reported to delay the onset of picrotoxin-included seizures in mice (Abdul-Ghani *et al*., 1987). The essential oil of the plant consists of Estragole and Eugenol (Zargari, 1989; Monod and Dortan, 1950) which are the major cause of anticonvulsant activity in *Pimpinella Anisum. L*. The anticonvulsant activity of estragole and eugenol has been reported by some researches like Dallmeier and Carlini (1981).

Due to vast variety of applications, extraction of the essential oil from this plant remained the subject of many studies. Conventional methods are based on using liquid extraction, but significant problems and limitations associated with these methods like environmental impacts and problems of organic solvents persuaded the researchers to search for alternatives like supercritical fluid extraction. Rodrigues *et* *al*. (2003) used SFE for extraction of essential oil from *Pimpinella Anisum L*. and reported the results.

SFE is often mathematically modeled to describe the extraction process and also to optimize the parameters which control the process. In general, modeling aims at simulating and automatically controlling industrial systems to improve technical, economical, and environmental aspects.

1.2 Background of Problem

SFE technique plays a dominating role in biomaterial processing, which enjoys the benefits of solvent properties of fluids near the critical point. During the separation process of Anise, adjusting the extractor pressure, feed mass, extraction time, etc, can modify the solvency properties of the supercritical fluid. But under the experimental conditions, it is very difficult and costly to obtain high pressure phase-equilibrium data.

In recent years, a number of researchers have studied SFE. Many papers were published to discuss the experimental set-ups, analyze the extraction process (e.g. Goto *et al*., 1993; Tonucci and Beecher, 1994; Favati *et al*., 1997; Clifford, 1998; Kaihara *et al*., 2002). Mathematical models are proposed by various authors (e.g., Cygnarowicz-Provost *et al*., 1992; Reverchon *et al*., 1993; Reverchon and Osseo, 1994; Reverchon and Poletto, 1996; Ago and Nishiumi, 1998)) to model SFE. In the conventional liquid extraction, equations of state are the most commonly used methods to analyze the system. For example, the Peng-Robinson (PR) equation of state (Peng, 1976) and the Soave modified Redlich-Kwong equation of state ((Soave, 1972); (Hollar, 1990)) are the most commonly used equations.

Researchers who investigated SFE followed similar approaches; however, serious problems are faced while developing a mathematical model for SFE. The most important problem is related to the lacking of understanding of the density parameter.

Because analytical models were not able to specify all aspects of SFE, a stepwise numerical modeling, called Artificial Neural Networks (ANN), has been applied. However, although ANN can be employed to solve a variety of problems, it has limitations, and there are still some issues associated with it.

Shokri *et al.* (2011) applied Artificial Neural Networks for modeling SFE of Anise. Although ANN can be employed to solve a variety of problems, there are still some problems associated with this method. The main drawbacks of ANN are:

i. Unable to read linguistic variables.
ii. Unable to manage imprecise or vague information.
iii. Unable to resolve conflicts.
iv. Rely on trial-and-error to determine hidden layers and nodes.
v. Difficult to reach global minimum error even by complex back-propagation (BP) planning.

Because of weaknesses of ANN, a proper model or correlation scheme to extend and complement the experimentally obtained data for SFE system at high pressures is useful. It can optimize the parameters to control the extraction process and also provide reliable prediction of the whole process.

Shokri *et* al. (2011) also applied mathematical modeling on SFE of Anise. Beside the general drawbacks of mathematical model, there is one considerable problem with the built mathematical model. The proposed mathematical model utilizes different collaborations for determining values of specific parameters like Sherwood number. Obviously, values which are calculated by the available collaborations cannot be completely true and useful for different conditions. This fact has inevitable effect on the performance of the built model. Removing this drawback from the mathematical model can significantly improve its performance.

On the other hand, ANN has also considerable problems. ANN fails to reach global minimum error which decreases the accuracy of the designed model in simulation and prediction. Besides, there are different conditions in which ANN cannot be employed like having linguistic variables or facing conflicts.

1.3 Problem Statement

The mentioned problems of ANN and Mathematical modeling have inevitable influence in the performance and reliability of the built models by these two methods in SFE field. The main aim of this study is to try to omit the mentioned problems and drawbacks in order to present models with promising performances. Models with the best performances will come up with more accurate simulations and predictions which accordingly, lead to excellent optimization in processes of SFE. The task of omitting problems is done by: (1) employing new method for modeling the process which does not have limitations of ANN, and (2) modifying the mathematical model and designing a hybrid model in order to improve the performance.

1.4 Objectives of Study

The purpose of this study is to develop an intelligent model for SFE of Anise using Neuro-Fuzzy approach which can be applied to industry and improve their productivity. The main objectives of this study are as follows:

1. Developing neuro-fuzzy model of supercritical fluid extraction of *Pimpinella anisum L* seed.
2. Building a gray box model for the process.
3. Validating the proposed models with experimental data.

1.5 Scope of Study

The boundary and scope of the study are as the followings:

i. Development of a neuro-fuzzy model to predict the mass of extract of Anise in industrial process of extraction. The complete process model is programmed and simulated in MATLAB R2010a environment.
ii. Training and validation of neuro fuzzy model by using industrial data.
iii. Developing a gray box model for the process.

1.6 Contribution of Study

Contribution of study is described as follows:

i. Since the process is quiet nonlinear, neuro fuzzy modeling brings advantages because of the capability to capture the nonlinear relationship between output and input elements for applications of SFE in industry.
ii. The neuro fuzzy model is able to predict the mass of extract, thus the excellent accuracy of the built model can be valuable.

1.7 Report Outline

i. Background and fundamental information about the research are elaborated in chapter 1.
ii. Chapter 2 provides complete description about *Pimpinella anisum*, process of supercritical fluid extraction, different artificial intelligence approaches for modeling, and concept of gray box.
iii. In chapter 3, the procedure of designing different neuro-fuzzy networks, the criteria by which they are compared to each other, and the way the gray box model is built, are explained.
iv. The results and discussions are presented in chapter 4.
v. Chapter 5 presents recommendations for further activities and researches.

REFERENCES

Abdul-Ghani, A. S., EI-Lati, S. G., Sacaan, A. I., Suleiman, M. S. (1987). Anticonvulsant effects of some Arab medicinal plants. *International Journal of Crude Drug Research* 25, 39-43.

Akinlua, A., Torto, N., Ajayi, T. R., (2008) Supercritical fluid extraction of aliphatic hydrocarbons from Niger Delta sedimentary rock. *Journal of Supercritical Fluids*. 45(1), 57-63.

Avicenna, A. (1988). Drugs and decoctions used in epilepsy. In: Sharafkandi, A. (Translator), Ghanoon Dar Teb, *Soroosh Press*, Tehran, pp. 242-246, 456-459.

Ago, K., Nishiumi, J. (1998). Calculation of mutual diffiusion near the critical region from peng-robinson equation of state. *Industrial Engineering Chemistry Research*. 37, 1692-1695.

Baysal, T., Ersus, S., Starmans, D. A.J., (2000). Supercritical extraction of β-carotene and lycopene from tomato paste waste. *Journal of Agriculture and Food Chemistry*. 48, 5507-5511.

Begum, S., Ahmed, M., Funk, P. and Xiong, N. (2010). Intelligent Signal Analysis Using Case-Based Reasoning for Decision Support in Stress Management. In Bichindaritz, I., Vaidya, S., Jain, A. & Jain, L. (Eds.) *Computational Intelligence in Healthcare 4* (Vol. 309, pp. 159-189)Springer Berlin / Heidelberg.

Behounek, L., Cintula, P. (2006). Fuzzy logics as the logic of chains. *Fuzzy Sets and Systems.* 157(5), 604-610.

Bezdek, J. (1981). *Pattern Recognition with Fuzzy Objective Function Algorithms*. New York: Plenum Press.

Bishop, C. M. (1995). *Neural Networks for Pattern Recognition*. Oxford University Press.

Boskababy.M.H, Ramazani-Assari.M., (2001). Relaxant effect of *Pimpinella Anisum* om isolated guinea pig tracheal chains and its possible mechanism(s). *Journal of Ethnopharmacol.*74, 83-88.

Bulsari, A. B. (1995). *Neural Networks for Chemical Engineers*. Elsevier Science Inc.

Cornelis, C., Deschrijver, G., Kerre, E. E. (2005). Advanced and challenges in interval-valued fuzzy logic. *Fuzzy Sets and Systems.* 156(5), 622-627.

Clifford, T. (1998). Fundamentals of Supercritical Fluids. *Oxford University Press. New York, USA.*

Cygnarowicz-Provost, M., O'Brien, D. J., Maxwell, R. J., Hampson, J. W. (1992) Supercritical fluid extraction of fungal lipids using mixed solvents:Experiment and modeling. *The Journal of Supercritical Fluids.* 5, 24-30.

Czogala, E., Leski, J. (2000). Fuzzy and neuro-fuzzy intelligent systems. *Heidelberg: Physuca-Verlag.* 141.

Dallmeier,K., Carlini, E.A., (1981). Anesthetic, hypothermic, myorelaxant and anticonvulsant effects of synthetic eugenol derivatives abd natural analogues. *Pharmacology*. 22, 113-127.

Ezzatzadegan, L. (2011). Neuro-fuzzy kinetik modeling of Propylene polymerization. *University Tecknoligi Malaysia.*

Favati, F., Galgano, F., Damiano, N., Lanazarini, G. (1997). Supercritical CO2 extraction of lycopene and B-carotene from by-product of the tomato industry. *Forth Italian Conference on Supercritical Fluids and their Applications.* 121-128.

Felfoldi-Gava, A., Szarka, S., Simandi, B., Blazics, B., Simon, B., Kery, A., (2012) Supercritical fluid extraction of *Alnus glutinosa* (L.) Gaertn. *Journal of Supercritical Fluids.* 61, 55-61

Goto. M, Sato. M, Hirose. T., (1993). Extraction of peppermint oil supercritical carbon dioxide. *Journal of Chemical Engineering of Japan.* 26, 59-68.

Gottwald, S.(2005) Mathematical aspects of fuzzy sets and fuzzy logic: Some reflections after 40 years. *Fuzzy Sets and Systems.* 156(3), 357-364

Gulcin, I., Oktay, M., Kirecci, E., Kufrevioglu, O. I. (2003). Screening of antioxidant and antimicrobial activities of anise (*Pimpinella Anisum L*) seed extracts. *Food Chemistry.* 83, 371-382.

Hagan, M. T., Demuth, H. B. and Beale, M. H. (1996). *Neural network design*. New Delhi: Vikas Publishing House Pvt. Ltd.

Hajek, P. (2006). What is mathematical fuzzy logic. *Fuzzy Sets and Systems.* 157(5), 628-634.

Hocaoglu, F. O., Oysal, Y., Kurban, M.(1999). Missing wind data forecasting with adaptive neuro-fuzzy inference system. *Neural Computations.* 18, 207-212.

Hollar, W. E., Ehrlich, P. (1990). Solubility of naphthalene in mixture of carbon dioxide and ethane. *Journal of Chemical Engineering Data*. 35, 271-275.

Jang, J. S. R. (1993). ANFIS: adaptive-network-based fuzzy inference system. *Systems, Man and Cybernetics, IEEE Transactions on*. 23(3), 665-685.

Jang, J. S. R. and Chuen-Tsai, S. (1995). Neuro-fuzzy modeling and control. *Proceedings of the IEEE*. 83(3), 378-406.

Jang, J. S. R., Sun, C. T. and Mizutani, E. (1997). Neuro-Fuzzy and Soft Computing-A Computational Approach to Learning and Machine Intelligence [Book Review]. *Automatic Control, IEEE Transactions on*. 42(10), 1482-1484.

Jovovic, M., Jonic, S. and Popovic, D. (1999). Automatic synthesis of synergies for control of reaching -- hierarchical clustering. *Medical Engineering & Physics*. 21(5), 329-341.

Kaihara, A., Yoshii, K., Tsumura, Y., Ishimitsu, S., Tonogai, Y. (2002). Multriresidue analysis of 18 pesticides in fresh fruits, vegetables and rice by supercrtical fluid extraction and liquid chromatography-electrosprayionization mass spectrometry. *journal of health Science. 48, 2.*

Kosalec, I., Pepeljnjak, S., Kustrak, D. (2005) Antifungal activity of fluid extract and essential oil from anise fruits (*Pimpinella Anisum L., Apiaceae*). *Acta pharmaceutica Zagreb Croatia.* 55(4), 377-385.

Lang, R. I. W. (2006). *A future for dynamic neural networks*, University of reading, UK.

Lucas, A.De., Rincon, J., Gracia, I. (2002). Influence of operating variables on yield and quality parameters of olive husk oil extracted with supercritical carbon dioxide. *Journal of the American oil Chemists'Society*. 79(3), 127-243.

Madaeni, S. S., Zahedi, G. and Aminnejad, M. (2008). Artificial neural network modeling of O2 separation from air in a hollow fiber membrane module. *Asia-Pacific Journal of Chemical Engineering*. 3(4), 357-363.

Mamdani, E. H., Assilian, S. (1975). An experiment in linguistic synthesis with a fuzzy logic controller. *International Journal of Man-Machine Studies*. 7(1), 1-13.

Ma, J., Chen, S., Xu, Y. (2006). Fuzzy logic from the veiwpoint of the machine intelligence. *Fuzzy Sets and Systems.* 157(5), 628-634.

McCulloch, W., Pitts, S. W., (1943). A logical calculus of the ideas immanent in nervious activity. *Bulletin of mathematical biophysics.* 9, 127-147.

Mezzomo, N., Martinez, J., Ferreira, S. R. S., (2009) Supercritical fluid extraction of peach (*Prunus persica*) almond oil: Kinetics, mathematical modeling and scale-up. *Journal of Supercritical Fluids*. 51(1), 10-16.

Monod, C., Dortan, D., (1950). Eugenol in anise oil. Chemical Abstracts 45, 3124i.

Nicholas, P. (2003). Industrial Solvents Handbook, Revised And Expanded. Cheremisinoff. eBook ISBN: 978-0-203-91133-4.

Novak, V. (2012). Reasoning about mathematical fuzzy logic and its future. *Fuzzy Sets and Systems.* 192, 25-44.

Oliveira, P. F., Machado, R. A. F., Bolzan, Ariovaldo, B., Barth, D. (2012). Supercritical fluid extraction of hernandulcin from *Lippia dulcis* Trev. *Journal of Supercritical Fluids.* 63, 161-168.

Oliveira, R., Rodrigues, M. F., Bernardo, M. G. (2002). Characterization and supercritical carbon dioxide extraction of walnut oil. *Journal of the American Oil Chemistry'Society*. 79(3), 225-230.

Orhan U., Hekim, M., Ibrikci, T. (2008). Gravitational fuzzy clustering. *Advances in Artificial Intelligence, Springer Berlin.* 524-531.

ÖZEL., A. (2009). Anise (*Pimpinella Anisum*): Changes in yields and component composition on harvesting at different stages of plant maturity. *Experimental Agriculture*. 45, 117-126.

Passos, C. P., Silva, R. M., Da Silva, F. A., Coimbra, M. A., Silva, C. M. (2009) Enhancement of the supercritical fluid extraction of grape seed oil by using enzymatically pre-treated seed. *Journal of supercritical fluids.* 48(3), 225-229.

Peng, D. Y., Robinson, D. B. (1976). A new two-constant equation of state. *Industrial Engineering Chemistry Fundamentals*. 15(1), 59-64.

Poliakoff, M., Meehan, N. J., Ross, S. K. (1999). A supercritical success story. *Chemistry and Industry.* 19, 750-752.

Potter, C. W., Negnevitsky, M. (2006). Very short term wind forecasting for Tasmanian power generation. *Power Systems,IEEE.* 21, 965-972.

Pourgholami. M.H, Javadi. M, Kamalinejad. M, Fanaee. G.H.R, Sayyah. M, (1999). The fruit essential oil of *Pimpinella Anisum* exerts anticonvulsant in mice. *Journal of Ethnopharmacology.* 66(2), 211-215.

Quah, J. T. S. and Ng, W. D. (2007). Utilizing Computational Intelligence for DJIA Stock Selection. *Proceedings of the 2007 Neural Networks, 2007. IJCNN 2007. International Joint Conference on*. 12-17 Aug. 2007. 956-961.

Reid, R. C., Prausnitz, J. M., Poling, B. E. (1987). The properties of gases and liquids. *New York: McGraw-Hill*. ISBN: 0070517991.

Reverchon, E., Poletto, M. (1996). Mathematical modeling of supercritical CO2 fractionation of flower concretes. *Chemical Engineering Science.* 51 (15), 3741-3753.

Reverchon, E., Osseo, L. S., (1994). Modeling of supercritical fluid extraction of basil oil. *Proceeding of the 3rd International Symposium of Supercritical Fluids, Strasbourg, France.*

Reverchon, E., Donsi, G., Osseo, L. S., (1993) Modeling os supercritical fluid extraction from herbaceous matrices. *Industrial Engineering Chemistry Research.* 32, 2721-2726.

Rodrigues, V. M., Rosa, P. T., Marques, M. O. M., Petenate, A. J., Meireless, M. A. A., (2003). Supercritical extraction of essential oil from Aniseed (*Pimpinella anisum* L) using CO_2: Solubility, Kinetics, and Composition Data.*Journal of Agriculture and Food Chemistry.* 51, 1518-1523.

Rozzi, N. L., Singh, R. K., Vierling, R.A, Watkins, B. A. (2002). Supercritical fluid extraction of lycopene from tomato processing byproducts. *Journal of Agriculture and Food Chemistry*. 50(9), 2638-2643.

Santos. P. M, F. A. C., Oliveira. M. M, Barroso. J. G, Pedro. L. G, Deans. S. G, Younus. A. K. M, Scheffer. J. J, (1998). Essential oils from hairy root cultures and from fruits and roots of *Pimpinella Anisum*. *Phytochemistry*. 48, 445-460.

Shankar, D. R., Kodali, A., Beerla, P. and Nimai, D. V. S. M. (2007). Neural Networks in Cultivation. *Proceedings of the 2007 Information Technology, 2007. ITNG '07. Fourth International Conference on*. 2-4 April 2007. 255-260.

Shokri, A., Hatami, T., Khamforoush, M. (2011). Near critical carbon dioxide extraction of Anise (*Pimpinella Anisum L.*) seed: Mathematical and artificial neural network modeling. *The Journal of Supercritical Fluids*. 58(1), 49-57.

Soave, G. (1972). Equilibrium constants from a modified redlich-kwong equation of state. *Chemical Engineering Science*. 27, 1197-1203.

Sugeno, M. and Kang, G. T. (1988). Structure identification of fuzzy model. *Fuzzy Sets Syst.* 28(1), 15-33.

Szekely, E., Simandi, B., Illes, R., Molnar, P., Gebefugi, I., Kmecz, I., Fogassy, E. (2004). Application of supercritical fluid extraction for fractionation of enantiomers. *Journal of Supercritical Fluids*. 31(1), 33-40.

Tabanca, N., Demirci, B., Ozek, T., Kirimer, N., Baser, K.H.C., Bedir, E., Khan, I.A., Wedge, D.E. (2006). Gas chromatographic-mass spectrometric analysis of essential oils from *Pimpinella* species gathered from Central and Northren Turkey. *Journal of Chromatography*. 1117(2), 194-205.

Takagi, T. and Sugeno, M. (1985). Fuzzy Identification of systems and its applications to modeling and control. *IEEE transactions on Systems, man, and Cybernetics*. 15(1), 116-132.

Tonucci, L. H., Beecher, G. R. (1994). Supercritical fluid extraction of carotenoids from tomato past. *5th International Symposium on Supercritical Fluid Chromatography and Extraction.*

The MathWorks Inc (2010). *Neural Network Toolbox*. The MathWorks, Inc.

Treybal. R.E (1990). Mass Transfer Operations. *3rd ed, McGraw-Hill, New York.*

Van Broekhoven, E., De Baets, B. (2009). Only smooth rule bases can generate monotone Mamdani-Assilian models under center of gravity defuzzification. *Fuzzy Systems, IEEE Transactions on.* 17(5), 1157-1174.

Wen-Yuan L., C.-J. X., Bao-Wen W., Yan S., Shu-Fen F. (2003). Study on combining subtractive clustering with fuzzy c-means clustering. *Machine Learning and Cybernetics, 2003 International Conference on.* 5, 2659-2662.

Williams, J. R., Clifford, A. A. (2000). Supercritical Fluid Methods and Protocols. *Humana Press*.

Yager, R. R. and Filev, D. P. (1994). Generation of Fuzzy Rules by Mountain Clustering. *Intelligent and Fuzzy Systems*. 2(3), 209-219.

Yang, C. T., Marsooli, R. and Aalami, M. T. (2009). Evaluation of total load sediment transport formulas using ANN. *International Journal of Sediment Research*. 24(3), 274-286.

Zadeh, L. A., (1973). Outline of a new approach to the analysis of complex systems and decision processe. *Systems, Man and cybernetics, IEEE.* 3(1), 28-44.

Zadeh, L. A. (1968). Fuzzy Algorithms. *Information and Contro.* 12(2), 94-102.

Zadeh, L. A. (1965). Fuzzy Sets. *Information and Control.* 8(3), 338-353.

Zahedi, G., Elkamel, A., Lohi, A., Jahanmiri, A. and Rahimpor, M. R. (2005). Hybrid artificial neural network--First principle model formulation for the unsteady state simulation and analysis of a packed bed reactor for CO2 hydrogenation to methanol. *Chemical Engineering Journal*. 115(1-2), 113-120.

Zahedi, G., Mohammadzadeh, S. and Moradi, G. (2008). Enhancing Gasoline Production in an Industrial Catalytic-Reforming Unit Using Artificial Neural Networks. *Energy & Fuels*. 22(4), 2671-2677.

Zahedi.G. , E. A., Lohi.A. ,Hatami. T. , (2010). Optimization of supercritical extraction of nimbin from neem seeds in presence of methanol as co-solvent. *supercritical fluids*. 55, 142.

Zargari, A., (1989). Medicinal Plants, vol. 2. Tehran University, Tehran, pp. 502-507.

Zeng, J. (2004). Modeling and Analysis of supercritical fluid extraction using soft computing based approaches. Thesis in Master of Science. University of Guelph.