Upgrading Atmospheric Residue by Simultaneous Employment of Ionic Liquid, Ultrasonic, and Thermal Cracking

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ABSTRACT: *In this study, the effect of simultaneous employment of ultrasonic wave radiation, chemical substance of ionic liquid, and operating conditions of thermal cracking is investigated experimentally on upgrading the Atmospheric Residue (AR) of a crude oil atmospheric distillation tower. The five main factors of this process that are investigated are ionic liquid concentration, ultrasonic wave power, ultrasonic radiation time, temperature, and pressure. According to Box-Behnken Design, 46 experiments are conducted. Then, the proper experimental condition of this process is determined and hence, based on Multilevel Categoric Design the efficiency of seven different kinds of ionic liquids is compared. According to this design, 14 experiments are conducted. The results of 46 experiments conclude that this process is able to upgrade AR and even the simultaneous employment of ionic liquid, ultrasonic and thermal cracking cause a synergistic effect on AR upgrading. Also, the results of 14 experiments indicate that 1-Propyl boronic acid-3-decylimidazolium bromide is a desirable ionic liquid for this process.*

KEYWORDS: *Atmospheric residue; Ionic liquid; Thermal cracking; Ultrasonic; Upgrading.*

INTRODUCTION

Approximately, one-third of oil refining content is residual [1]. Heavy components and complex compositions in residual oil have a negative effect on the refining processes [2] and increase refining costs [3]. Therefore, the importance of residual oil processing is increasing day by day [4, 5]. One of the upgrading methods is the cracking process [6]. Nowadays, AR is cracked by one of the following processes: thermal cracking, catalytic cracking, hydrocracking, and modern methods of cracking.

In the thermal process, cracking is occurred at high

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pressure and temperature, i.e. in the range of 7E+5 to 70E+5 Pa and 723.15 to 823.15 K [7], but one of the disadvantages of this process is the formation of free radicals [8]. Although the catalytic cracking process has some advantages compared to the thermal process [9-12], the fouling of catalysts during this process is an important and significant problem [13]. Similar to the thermal cracking process, the hydrocracking process cracks heavy components at high pressure and temperature [14-16]. The disadvantages of this process are high pressure and temperature conditions and the fouling of catalysts during this process [13, 17]. Up to now, some new methods of residue cracking are suggested and investigated experimentally such as using solvents, ultrasonic, microwave, etc. However, in this section, only experimental methods which are similar to the suggested process in this study are introduced. These methods are residue cracking by ionic liquids, ultrasonic, ultrasonic-assisted-ionic liquids, and thermal cracking-assisted-ultrasonic.

According to previous studies, some chemical substances [3] such as ionic liquids have a positive effect on heavy oil upgrading [18-24]. In this way, ionic liquids crack the long-chain molecules of residuals by chemical reactions [25-29]. While *Villanueva et al.* concluded that ionic liquids have high thermal stability [30]; *Nares et al.* concluded that the disadvantage of this process is the long operating time [18]. Nowadays, some advantages like equipment simplicity, easy operation, low price, and being environmentally friendly cause ultrasonic to be the focus of attention [31-33]. According to the literature, ultrasonic is a useful way for residual oil cracking [2, 34-44], desulfurization [45], and other goals of oil upgrading. Also, it can be used as an alternative or intensifier of some chemical reactions [46, 47]. The results reveal that the blending of additives with external energy [48] such as ionic liquid and ultrasonic radiation causes a synergistic effect [38, 49]. Also, according to previous studies, the process of unconventional thermal cracking such as simultaneous use of ultrasonic and thermal cracking upgrades oil more than conventional thermal cracking processes [50, 51]. According to the mentioned studies, ionic liquid, ultrasonic, thermal cracking, thermal cracking-assisted-ultrasonic, and ultrasonic-assisted-ionic liquid are feasible, but high pressure and long duration are the main problems of operating conditions [18, 51].

In this study, a process of AR cracking is suggested and investigated experimentally. This process uses ultrasonic wave radiation, chemical substance of ionic liquid, and operating conditions of thermal cracking, simultaneously, followed by determining the proper experimental conditions of this process. In other words, the effort is made to investigate whether the employment of three processes of atmospheric residue upgrading simultaneously improves the operating conditions and efficiency of upgrading compared to conventional processes or not. Then, in the proper condition, the efficiency of seven different kinds of ionic liquids on AR cracking is compared. In other words, an attempt is made to select the effective ionic liquid, among seven different kinds of ionic liquids, to crack AR by simultaneous employment of ultrasonic, ionic liquid, and thermal cracking. Meanwhile, all experiments are statistically designed, and their results are statistically and technically analyzed.

EXPERIMENTAL SECTION

Experimental Set-up

As shown in Fig. 1, the experimental apparatus, which is built for this study consists of a double-glazed batch reactor which is made of stainless steel AISI 316L and its internal volume is about 10 L while its external height and radius are about 0.4 m and 0.15 m, respectively. Pressure and temperature ranges are 1E+5 to 10E+5 Pa and 293.15 to 473.15 K, respectively. Nitrogen gas, valve actuator, air compressor and pressure transmitter are used to adjust the pressure of the reactor. Also, the heating element, Pt100 resistance temperature detector, and a condenser that is connected to the annulus between the internal and external shells of the reactor and also connected to the annulus between the internal and external shells of the double-glazed cooling tower at the top of the reactor's door are used to adjust the temperature of the reactor. An automatic stirrer is employed in the apparatus and is located in the reactor. Also, an ultrasonic generator which can operate at 20 kHz frequency and a power range of 50 to 5000 W, and its probe is made of Titanium, is employed in the apparatus. In the apparatus, a condenser is connected to both generator and probe in order to cool them with cold water while two jet motor fans are used to cool piezoelectrics by an intensive air blow. A finger touch monitor is also employed in the apparatus to adjust power, pressure, temperature, and time.

Table 1: Factors and ranges.

Factor	Unit	Low level	High level
Ionic liquid concentration (C)	part per million (ppm)	1	150
Ultrasonic wave power (P_w)	Watt (W)	50	5000
Ultrasonic radiation time (t)	second (s)	40	4000
Temperature (T)	Kelvin (K)	293.15	463.15
Pressure (P)	Pascal (Pa)	100000	800000

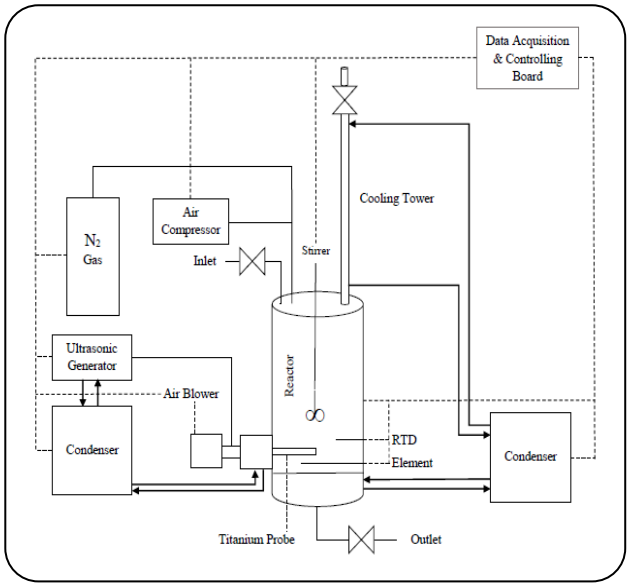

Fig. 1: Schematic view of the apparatus.

Statistical Design of Experiments

In this study, an attempt is made to investigate the effect of five factors on decreasing the density of AR by this process. Box-Behnken Design is used to design the experiments statistically by the 10th version of Design-Expert software [52]. The Design–Expert is a statistical software package from Stat-Ease Inc., which is specifically dedicated to performing experimental design. It should be mentioned that Box-Behnken designs are used to generate higher-order response surfaces using fewer required runs than a normal factorial technique [53]. Also, Box-Behnken design usually has fewer design points than central composite design; thus, it is less expensive to run with the same number of factors.

The factors and their ranges are mentioned in Table 1.

According to this design method, forty-six experiments should be carried out consisting of forty experiments in the mentioned ranges in Table 1, while six are replicated at the center of these ranges. Meanwhile, three liters of AR are used for each experiment. Then, to investigate AR upgrading after each experiment, AR density is measured by the density meter instrument (DMA-4100, Anton Paar Co., Austria) at 288.70 K. In other words, in order to investigate the feasibility of the suggested process, forty-six experiments should be carried out, for which the result of each experiment is the ultimate density of AR. It should be noted that the initial density of the supplied AR by the oil refinery is 960.5 kg/m^3 at 288.70 K.

Then the proper experimental condition of the process is statistically determined and finally, the efficiency of seven kinds of ionic liquids on AR density is investigated and the desirable ionic liquid to achieve minimum AR density is selected. In this step, Multilevel Categoric Design is used for the design of the experiments statistically by the Design-Expert software. The name and molecular formula of ionic liquids are mentioned in Table 2.

It should be mentioned that imidazolium-based ionic liquids not only possess the extraordinary physicochemical properties of ionic liquids but also have excellent basicity and surface activity [54]. Each mentioned ionic liquid has been experimented on twice. In other words, in order to increase the accuracy of the results, the seven experiments are doubled checked; therefore, fourteen experiments are carried out. Also, three liters of AR are used in each experiment, and after each experiment, the density of AR is measured by the mentioned instrument. In other words, to compare the efficiency of mentioned ionic liquids on AR density, fourteen experiments should be carried out, for which the result of each experiment is the ultimate density of AR.

Overall, in order to analyze the suggested process, 46 experiments should be conducted, and thereafter to compare the efficiency of the mentioned ionic liquids in the process, 14 experiments should be conducted. After

Table 2: List of ionic liquids.

No.	Name	Molecular Formula
1	1-(2-hydroxyethyl)-3-methylimidazolium chloride	$C_6H_{11}ClN_2O$
2	1-(2-hydroxyethyl)-3-methylimidazolium nitrate	$C_6H_{11}N_3O_4$
3	1-octyl-3-methylimidazolium chloride	$C_{12}H_{23}ClN_2$
4	1-octyl-3-methylimidazolium nitrate	$C_{12}H_{23}N_3O_3$
5	1-butylimidazolium nitrate	$C_7H_{13}N_3O_3$
6	1-Butyl-3-methylimidazolium tetrafluoroborate	$C_8H_{15}BF_4N_2$
7	1-Propyl boronic acid-3-decylimidazolium bromide	$C_{16}H_{32}BBrN_2O_2$

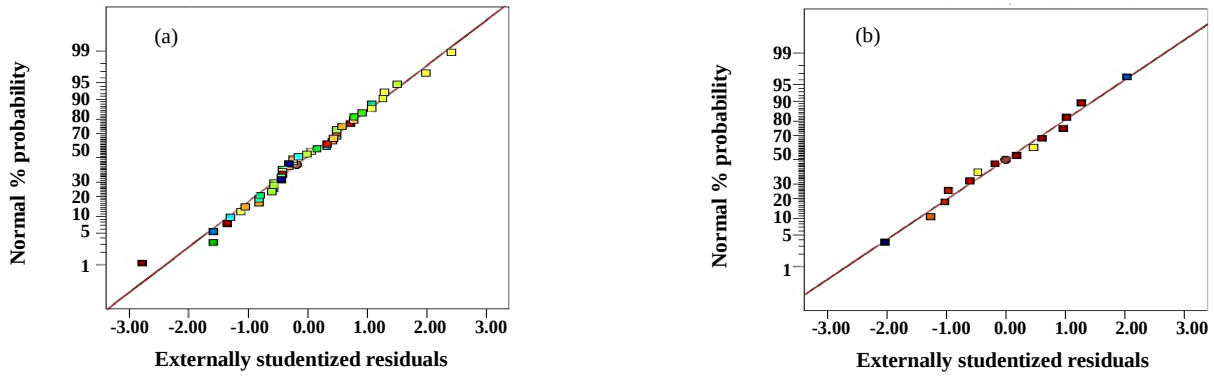

Fig. 2. Normal probability plot of residuals for a.46-experiment, b.14-experiment.

conducting all experiments and before technically analyzing the results, the validity of all experimental results should be statistically checked and verified.

Statistical analysis of the results of experiments

According to statistical concepts, all experimental results should be checked and verified by the plots as follows:

Normal probability plot of residuals to check for the normality of residuals [52]

The residual of each run is related to the difference between the ultimate AR density obtained experimentally and obtained statistically. This plot implies whether the residuals are in normal distribution which means the residuals follow a straight line or not. Formal statistical tests are not used for this diagnostic; therefore, visual inspection of the graph is sufficient. Fig. 2 demonstrates that residuals of 46 and 14 experiments are normally distributed which means that the difference between experimental results and the statistical results is always constant.

Residuals versus Run plot to check for lurking variables [52]

This plot provides a check for lurking variables that may have influenced the response during the experiment. The plot should show a random distribution. This plot is also used to examine outliers. Outliers are run with residuals outside the red lines on the plot. An outlier is an observation that is not fit well with the model. This indicates that either the observation is problematic or the wrong model has been used, or a combination of both has occurred. As can be seen in Fig. 3, the residuals of 46 and 14 experiments are randomly distributed and none of them is out of range which means that all experimental results are valid.

DFFITS versus run plot to look for outliers [52]

DFFITS stands for "difference in fits". It is calculated by measuring the change in predicted values that occurs when that response value is deleted. The larger the value of DFFITS, the more it influences the fitted model. A run is considered influential when the value of the DFFITS is outside the limits. In other words, the DFFITS plot can be

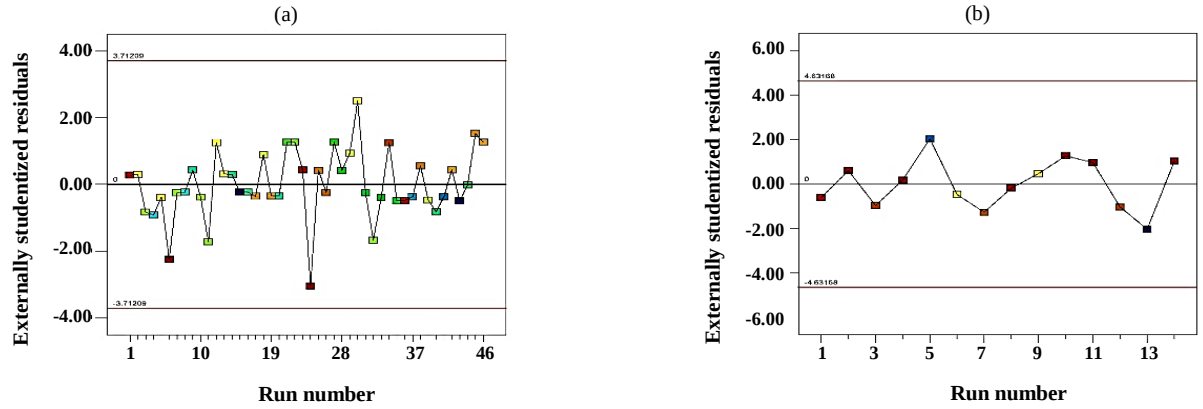

Fig. 3: Residuals vs. Run plot for a.46-experiment, b.14-experiment.

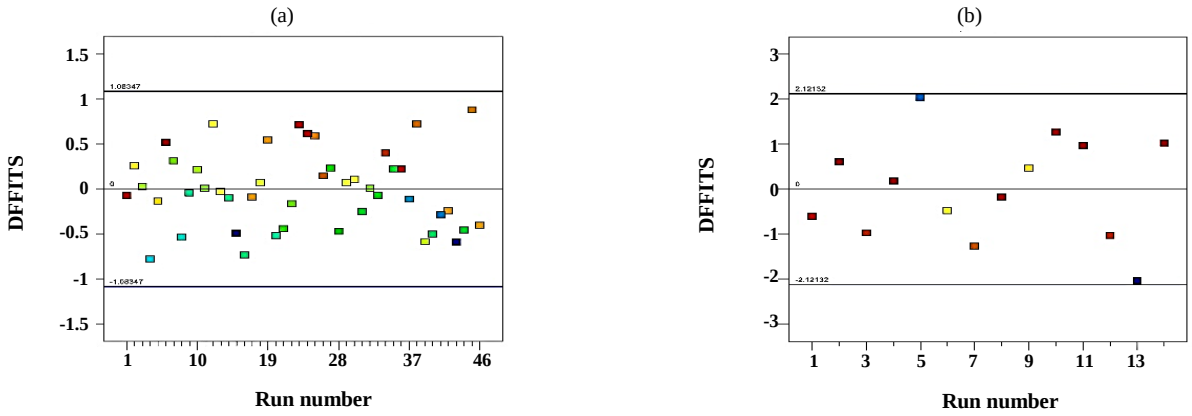

Fig. 4: DFFITS vs. Run plot for a.46-experiment, b.14-experiment.

used to judge the influence of suspected outliers. Fig. 4 indicates that all of the DFFITS values of 46 and 14 experiments are in the range and have not exceeded the blue lines which means that none of the experimental results are invalid.

According to these plots, all experimental results are correct and valid; and none of the experiments need to be repeated.

RESULTS AND DISCUSSION

After confirmation of all results by mentioned plots, it is statistically adequate to technically analyze the experimental results.

Process Analysis

According to the 46 experimental results and based on the Box-Behnken Design, the Design-Expert software yields a statistical model. According to the value of "p-value Prob > F" for the model, mentioned in Table 3, there is a 0.01% chance that the response occurs due to noise [52]. It technically means that the difference between the results of all 46 experiments is due to the use of the process in different experimental conditions; i.e. this suggested process is effective in decreasing the AR density.

Also, the significance of a parameter depends on its value of "p-value Prob > F"; i.e. if it is less than 0.0500 then that parameter is significant [52]. In this process, C, P_w, t, T, P, C.P_w, C.t, C.T, C.P, P_w.t, P_w.T, P_w.P, t.P, T.P, $C^{2,}$ and T^2 are significant which means that these parameters are effective in AR density reduction by this process. The statistical model in terms of coded factors belonging to this process is:

$$\rho^3 = 10^7 \times (81.75 - 0.6543 \times C - 0.6464 \times P_w + 1.598 \times t - 5.889 \times T - 1.902 \times P - 4.484 \times C \times Pw + 5.060 \times C \times t - 0.8532 \times C \times T + 6.224 \times C \times P + 1.232 \times P_w \times t - 3.418 \times P_w \times T + 2.439 \times Pw \times P - 4.629 \times t \times P - 2.715 \times T \times P - 0.5296 \times C^2 - 2.091 \times T^2 \quad (1)$$

Table 3: ANOVA table of the process (46-experiment).

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	1.241E+017	20	6.206E+015	128.13	< 0.0001	significant
C	6.849E+014	1	6.849E+014	14.14	0.0009	
Pw	6.685E+014	1	6.685E+014	13.80	0.0010	
t	4.086E+015	1	4.086E+015	84.35	< 0.0001	
T	5.549E+016	1	5.549E+016	1145.59	< 0.0001	
P	5.790E+015	1	5.790E+015	119.53	< 0.0001	
C.Pw	8.043E+015	1	8.043E+015	166.06	< 0.0001	
C.t	1.024E+016	1	1.024E+016	211.41	< 0.0001	
C.T	2.912E+014	1	2.912E+014	6.01	0.0215	
C.P	1.550E+016	1	1.550E+016	319.93	< 0.0001	
Pw.t	6.073E+014	1	6.073E+014	12.54	0.0016	
Pw.T	4.672E+015	1	4.672E+015	96.47	< 0.0001	
Pw.P	2.379E+015	1	2.379E+015	49.12	< 0.0001	
t.T	3.990E+012	1	3.990E+012	0.082	0.7765	
t.P	8.572E+015	1	8.572E+015	176.99	< 0.0001	
T.P	2.948E+015	1	2.948E+015	60.88	< 0.0001	
C^2	2.447E+014	1	2.447E+014	5.05	0.0336	
Pw^2	1.229E+014	1	1.229E+014	2.54	0.1238	
t^2	1.993E+011	1	1.993E+011	4.115E-003	0.9494	
T^2	3.816E+015	1	3.816E+015	78.78	< 0.0001	
P^2	1.534E+014	1	1.534E+014	3.17	0.0873	
Residual	1.211E+015	25	4.843E+013			
Lack of Fit	6.901E+014	20	3.450E+013	0.33	0.9656	not significant
Pure Error	5.208E+014	5	1.042E+014			

According to the sign of each parameter in this equation, C, P_w, T, P, C.P_w, C.T, P_w.T, t.P, T.P, $C^{2,}$ and T^2 have a positive effect while t, C.t, C.P, P_w.t, and P_w.P have a negative effect on decreasing AR density by this process. Also, according to the coefficient of each parameter in this equation, C.P is the most effective parameter and after that T, C.t, t.P, C.P_w, P_w.T, T.P, P_w.P, P, T^2, t, P_w.t, C.T, C and P_w are effective, respectively. Three technical results from the statistical model are as follows:

1- Since C, P_w, T, P, C.P_w, C.T, P_w.T, T.P, $C^{2,}$ and T^2 have a positive effect on the process; therefore, it can be concluded that simultaneous employment of ionic liquid, ultrasonic, and thermal cracking causes a synergistic effect on AR upgrading.

2- Since t, C.t, and P_w.t have a negative effect on the process while C and P_w have a positive effect, it is concluded that this process can operate better in a short time (fewer values of t).

3- Since C.P is the most effective parameter of the process and additionally, C.P and P_w.P have a negative effect while C and P_w have a positive effect, it is concluded that this process can operate better at low pressure (fewer values of P).

Accordingly, in the range of each main factor which is mentioned in Table 1, the suggested process is more effective in the reduction of AR density than similar processes of cracking, i.e. cracking via ionic liquid, ultrasonic, thermal cracking-assisted-ultrasonic, and ultrasonic-assisted-ionic liquid. Also, this process is better than the processes of upgrading with the presence of ionic liquids, due to the short time of upgrading AR. This process is also better than the processes of upgrading by thermal cracking, due to an upgrade of AR at atmospheric pressure.

According to the model, the proper experimental condition of the process, which is determined by the software, is graphically depicted in Fig. 5.

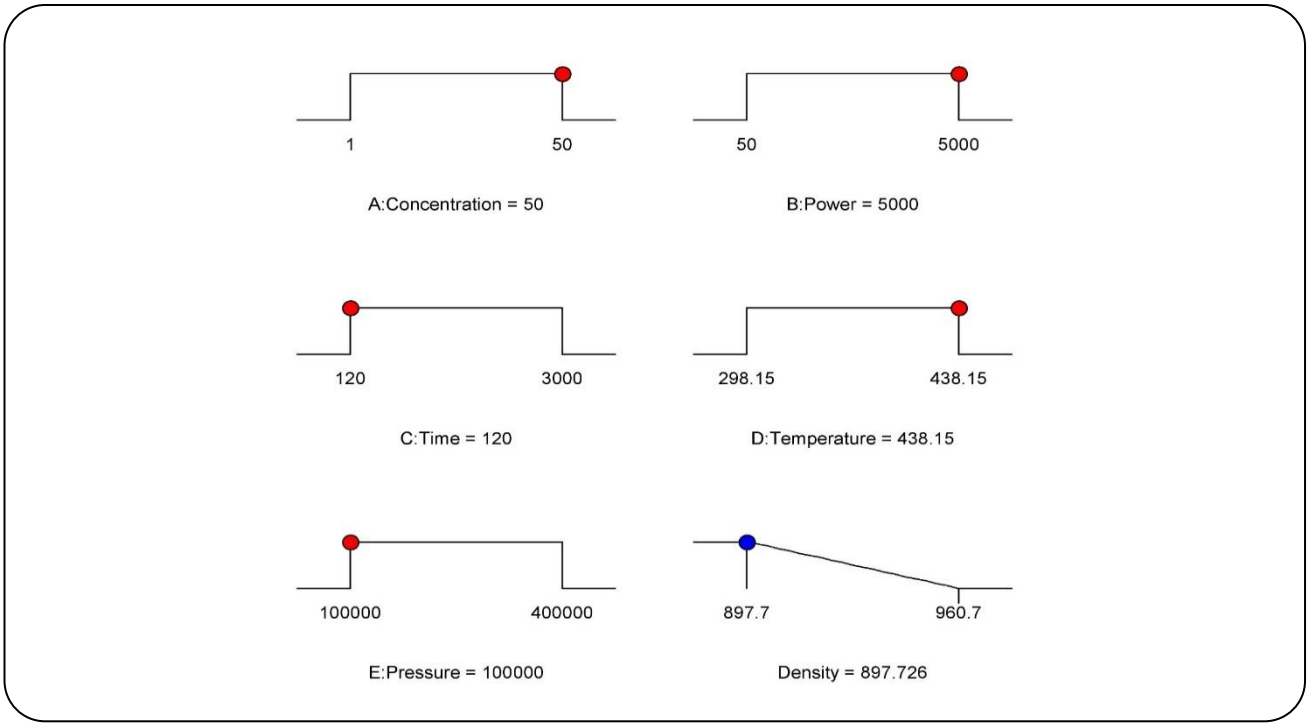

Fig. 5: The proper experimental condition of the process.

According to this figure, the proper condition of the process is when ionic liquid concentration is equal to 50 ppm, ultrasonic wave power is equal to 5000 W, ultrasonic radiation time is equal to 120 s, the temperature is equal to 438.15 K and pressure is equal to 100000 Pa, simultaneously. Meanwhile, in the mentioned condition, the AR density is equal to 897.7 kg/m^3 at 288.70 K. In other words, in this condition, the density of AR reduces from the initial value (960.5 kg/m^3 at 288.70 K) to 897.7 kg/m^3 at 288.70 K.

Technical and Statistical Comparison of the Ionic Liquids

According to the 14 experimental results and based on the Multilevel Categoric Design, the Design-Expert software yields a statistical model. According to the value of "p-value Prob > F" for the model, mentioned in Table 4, there is a 0.01% chance that the response occurs due to noise [52]. It technically means that the difference between the results of all 14 experiments is due to the use of the process in different experimental conditions; i.e. the kind of ionic liquid is effective in decreasing the AR density.

According to the results of the 14 experiments, the ionic liquids mentioned in Table 2 can be compared pairwise according to their ability of upgrading AR, as mentioned in Table 5. In this table, the difference between the two treatments is significant when the values of "Prob > |t|" are less than 0.0500 [52]. As it is observed from this table, the efficiency of ionic liquid numbers 1, 2, 3, 4, and 5, which are 1-(2-hydroxyethyl)-3-methylimidazolium chloride, 1-(2-hydroxyethyl)-3-methylimidazolium nitrate, 1-octyl-3-methylimidazolium chloride, 1-octyl-3-methylimidazolium nitrate, and 1-butylimidazolium nitrate, respectively, are significantly different from ionic liquid numbers 6 and 7, which do not yield a sensible difference. Meanwhile, the efficiency of ionic liquid numbers 6 and 7, which are 1-Butyl-3-methylimidazolium tetrafluoroborate and 1-Propyl boronic acid-3-decylimidazolium bromide, respectively, are significantly different from each other.

The One Factor Effects graph indicates the linear effect of changing the level of a single factor, as shown in Fig. 6. For factorial analysis, the least significant difference (LSD) calculations cause the I-beams around the predictions. The LSD I-beams are approximate tests to investigate whether the predictions at the displayed factor combinations are significantly different or not [52].

According to this figure, the ionic liquid number 7 is more effective than the ionic liquid number 6, and actually, the most effective ionic liquid, among the seven ionic liquids mentioned in Table 2, for reducing AR density is 1-Propyl boronic acid-3-decylimidazolium bromide.

Table 4: ANOVA table (14-experiment).

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob> F	
Model	2.452E+016	6	4.087E+015	68.41	< 0.0001	significant
A-Ionic Liquid	2.452E+016	6	4.087E+015	68.41	< 0.0001	
Pure Error	4.182E+014	7	5.974E+013			

Table 5: Ionic liquids comparison table.

Treatment	Mean Difference	df	Standard Error	t for H_0 Coeff=0	Prob > |t|
1 vs 2	-2.914E+006	7	7.729E+006	-0.38	0.7173
1 vs 3	-8.498E+006	7	7.729E+006	-1.10	0.3079
1 vs 4	-5.569E+006	7	7.729E+006	-0.72	0.4946
1 vs 5	-2.384E+006	7	7.729E+006	-0.31	0.7667
1 vs 6	2.430E+007	7	7.729E+006	3.14	0.0163
1 vs 7	1.169E+008	7	7.729E+006	15.13	< 0.0001
2 vs 3	-5.584E+006	7	7.729E+006	-0.72	0.4935
2 vs 4	-2.654E+006	7	7.729E+006	-0.34	0.7414
2 vs 5	5.304E+005	7	7.729E+006	0.069	0.9472
2 vs 6	2.722E+007	7	7.729E+006	3.52	0.0097
2 vs 7	1.198E+008	7	7.729E+006	15.51	< 0.0001
3 vs 4	2.929E+006	7	7.729E+006	0.38	0.7159
3 vs 5	6.114E+006	7	7.729E+006	0.79	0.4549
3 vs 6	3.280E+007	7	7.729E+006	4.24	0.0038
3 vs 7	1.254E+008	7	7.729E+006	16.23	< 0.0001
4 vs 5	3.185E+006	7	7.729E+006	0.41	0.6926
4 vs 6	2.987E+007	7	7.729E+006	3.86	0.0062
4 vs 7	1.225E+008	7	7.729E+006	15.85	< 0.0001
5 vs 6	2.669E+007	7	7.729E+006	3.45	0.0106
5 vs 7	1.193E+008	7	7.729E+006	15.44	< 0.0001
6 vs 7	9.263E+007	7	7.729E+006	11.98	< 0.0001

CONCLUSIONS

In this study, an attempt is made to investigate the efficiency of the process of AR upgrading. Also, it is attempted to select the desirable ionic liquid, between seven different kinds of ionic liquids, to upgrade AR by this process. It should be mentioned that in this study all experiments are statistically designed by the 10^{th} version of the Design-Expert software, and their results are statistically and technically analyzed. To analyze the process, based on Box-Behnken Design, 46 experiments are conducted, and then to compare the efficiency of the mentioned ionic liquids on the process, based on Multilevel Categoric Design, 14 experiments are conducted.

The results of 46 experiments conclude that the process is able to upgrade AR and even the simultaneous employment of ionic liquid, ultrasonic, and thermal cracking causes a synergistic effect on AR upgrading; accordingly, this process is more effective than similar processes of upgrading, i.e. upgrading via ionic liquid, ultrasonic, thermal cracking-assisted-ultrasonic and

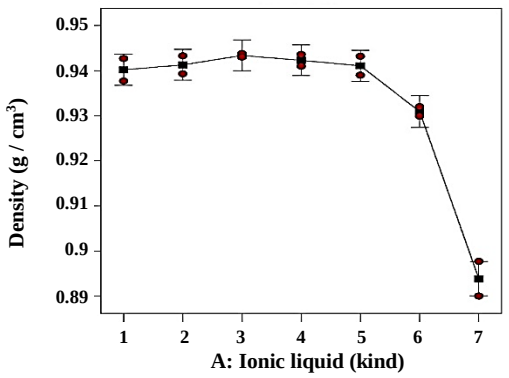

Fig. 6: One-factor effects plot.

ultrasonic-assisted-ionic liquid. Also, Ionic liquid concentration, ultrasonic wave power, ultrasonic radiation time, temperature and pressure, and all two-factor interactions except time-temperature interaction (t.T) are effective parameters of the process.

The results of 14 experiments indicate that 1-(2-hydroxyethyl)-3-methylimidazolium chloride, 1-(2-hydroxyethyl)-3-methylimidazolium nitrate, 1-octyl-3-methylimidazolium chloride, 1-octyl-3-methylimidazolium nitrate, and 1-butylimidazolium nitrate do not have a significant effect on the process. 1-Butyl-3-methylimidazolium tetrafluoroborate has a minor effect on the process. 1-Propyl boronic acid-3-decylimidazolium bromide is the most effective ionic liquid to crack AR in this process.

Nomenclatures

ANOVA	Analysis of variance
AR	Atmospheric residue
df	Degree of freedom
DFFITS	Difference in fits
LSD	Least significant difference
Prob	Probability
K	Kelvin
kg/m^3	Kilogram per cubic meter
kHz	Kilohertz
L	Liter
m	Meter
Pa	Pascal
ppm	part per million
s	Second
W	Watt
C	Concentration
P_w	Power of ultrasonic waves
P	Pressure
t	Time
T	Temperature
$C.P_w$	Concentration-power of ultrasonic waves interaction
C.t	Concentration-time interaction
C.T	Concentration-temperature interaction
C.P	Concentration-pressure interaction
P_w.t	Power of ultrasonic waves-time interaction
P_w.T	Power of ultrasonic waves-temperature interaction
P_w.P	Power of ultrasonic waves-pressure interaction
t.T	Time-temperature interaction
t.P	Time-pressure interaction
T.P	Temperature-pressure interaction

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