

Hydrodesulfurization of Syrian Gas-Oil over Cobalt Molybdenum Catalyst

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ABSTRACT. Hydrodesulfurization of gas-oil is a very important process in Syrian refining industry. This product contains high percentage of sulfur. It is used widely for heating and transport. The presence of sulfur causes serious pollution and corrosion problems. This study investigates the influence of various variables on the hydrodesulfurization of heavy Syrian gas oil over Cobalt Molybdenum catalyst. The results obtained showed an increase in conversion with the increase in temperature in the range 360-420°C. The reaction was found to follow a second order kinetics. Pressure increases the conversion up to a certain level and then the influence is less marked.

1. Introduction

Syrian crude contains 4-5% by weight sulfur. It is in this respect one of the richest in sulfur in the world. It is necessary for pollution, corrosion and further catalytic conversions to hydrodesulfurize the various end-products. Hydrodesulfurization of Gas-oil and fuel-oil is especially important since most of the sulfur in the crude remains in these heavy cuts. The hydrodesulfurization is also more difficult requiring special catalysts, higher H_2/HC ratios and more severe operating conditions. This study investigates the influence of various operating variables on the hydrodesulfurization of Syrian gas-oil over Cobalt-Molybdenum catalyst in a pilot - plant unit.

2. Experimentals

Experiments were carried out on gas-oil from topping units treating Syrian crudes. This gas-oil has the following properties:

Molecular weight	257 gm/mole
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Density at 20°C	.95 gm/cm ³
Specific gravity API	17.44
IBP at 0.1 bar	60°C
Temp of 50% at 0.1 bar	290°C
Temp of 50% at Atm	385°C
Sulfur wt %	4.2%

The gas-oil was mixed with n-heptane on 1:1 ratio in order to facilitate the flow in the unit. The molecular weight of the mixture was calculated and found to be 155 gm/mole. The percentage of sulfur 2.44%. The catalyst used was supplied from IFP for hydrotreating units in Home Refinery Syria. It has the following properties:

Volume of catalyst	230 ml
Outside diameter	3 mm
Specific Area	280 ± 30 m ² /Kg
Density	0.6 gm/cm ³
Specific Vol.	0.65 ± 0.05 cm ³ /gm
Losses due to friction	< 2%
Mo O ₃ = 12% wt. Co O = 2.2% wt. Na ₂ O < 700 ppm, Fe ₂ O ₃ < 400 ppm, Al ₂ O ₃ support, Losses at 550°C	< 1% wt.

The catalyst was activated for 48 hours at a temp of 200°C and under H₂ pressure of 1 atm. The pilot-plant used is illustrated in Fig. (1). A metering piston pump was used to pump the liquid into the reactor. The flow was accurately controlled in the range of 3-7 ml/min. The reactor was purged by N₂ and then H₂ was admitted and heated by liquid Lead in the preheater. The Hydrogen flow used was in the range 3-6 N liter/min and the pressure was fixed at 50 bars. The preheater heats the gas and liquid separately. The gas and liquid were mixed before entering the reactor. This consists of four sections which are electrically heated and with a temp control. The gas flows as a continuous phase while liquid is sprayed to form a film over the catalyst. The gas and liquid products go to a cooler, then to a filter and then to a non-return valve and finally to a high pressure separator. The mixture is further cooled in a cooling separator (water and methanol) then to a second separator.

Gas continues to atmosphere through a sampling chamber. Liquid samples were withdrawn from the separator. Gas samples were taken from the sampling chambers. Liquid samples were analysed by the usual ASTM methods including sulfur determination by Quartz-tube method ASTM D1551.

3. Results

3.1 Influence of Temperature

3.2 Influence of space velocity

They show an increase in conversion with a decrease in space velocity. The range of space velocities are 1-1.75 hr⁻¹ Fig. (4) is a plot of concentration of sulfur

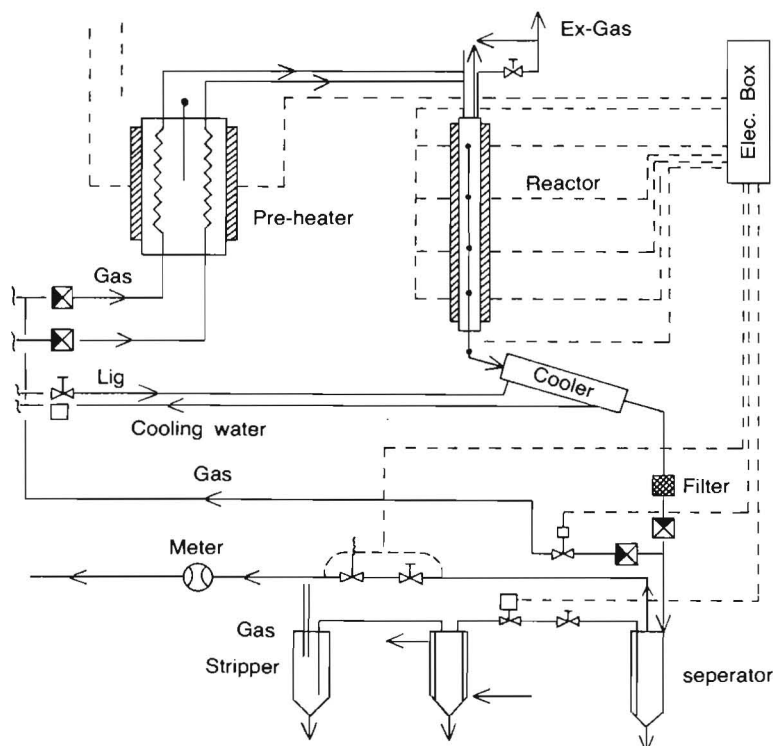


Fig. 1. Hydrodesulfurization Pilot-plant unit

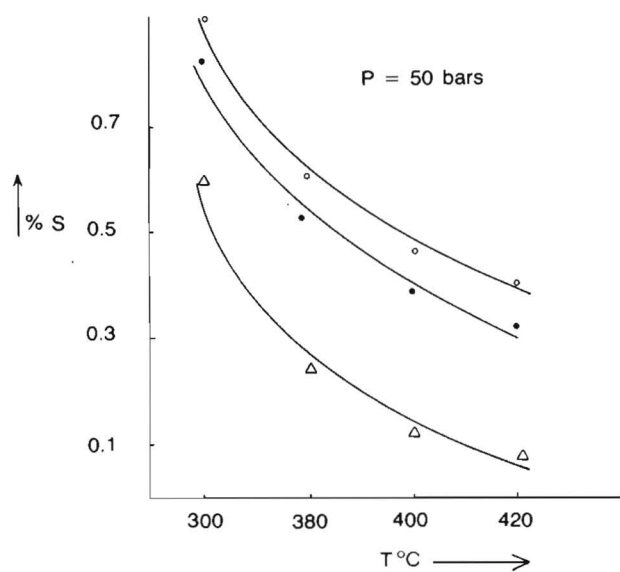


Fig. 2. Effect of temperature

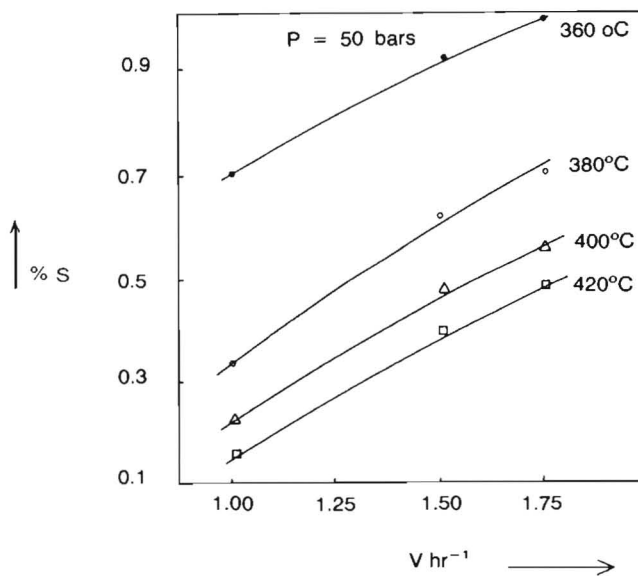


Fig. 3. Effect of Space Velocity

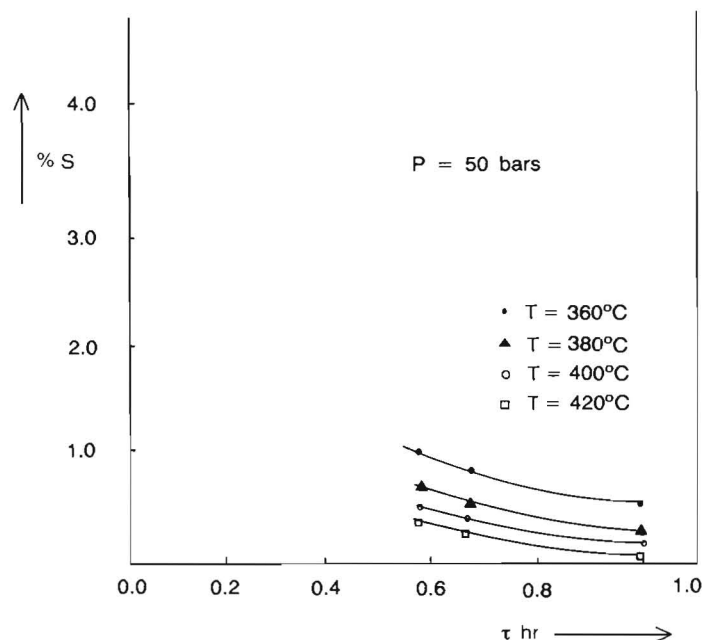


Fig. 4. Effect of Residence Time

in product against residence time. Fig. (5) is a plot of $\text{Log } \frac{1}{1-x}$ v.s. residence time at different temps, where x is the fraction of sulfur compounds converted at certain time. The curves are approximately straight lines.

3.3 Influence of Pressure

Fig. (6) shows the influence of pressure on the conversion of sulfur compounds. The pressures investigated are in the range 20-60 bars. It shows an increase in conversion with increase in pressure. This influence steadies off at high pressures. Fig. (7) is a plot of $\text{Log } \frac{1}{1-x}$ v.s. pressure.

4. Discussion of Results

The temperature influences the velocity of the reaction according to the Arrhenious equation:

$$k = k_0 e^{-E/RT}$$

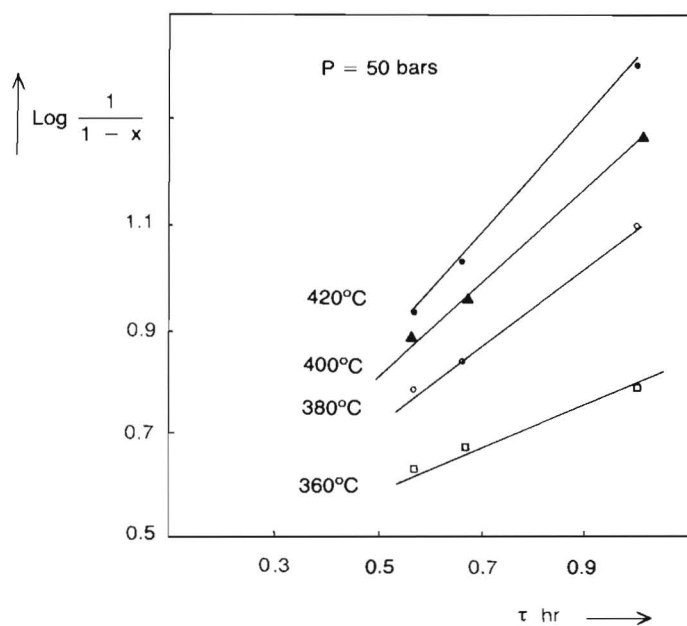


Fig. 5. Effect of Residence Time

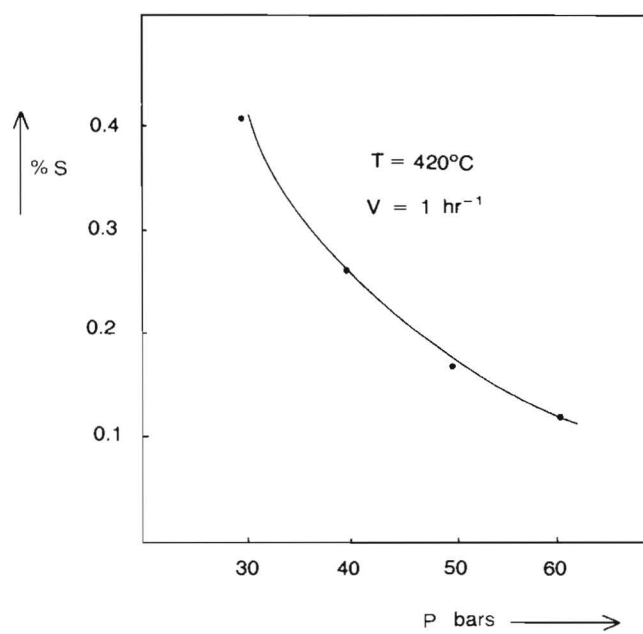


Fig. 6. Effect of Pressure

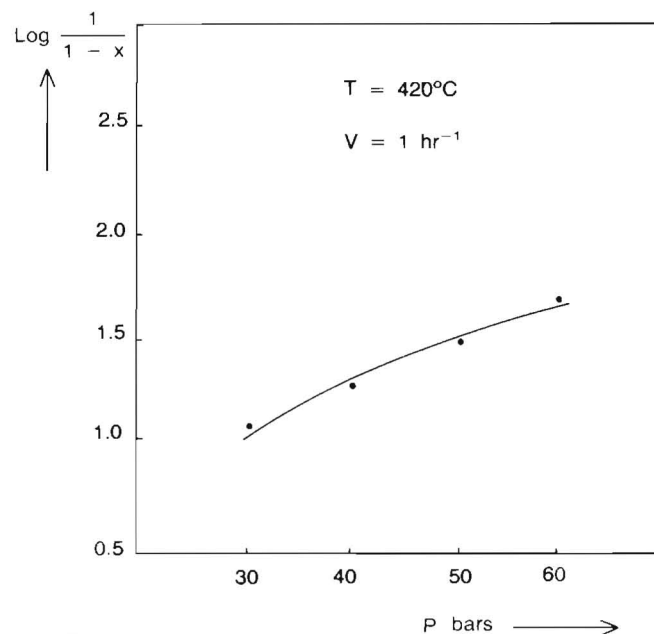


Fig. 7. Effect of Pressure

The reaction is possible thermodynamically at moderate temps. but under 360°C it is very slow. It is clear from Fig. (2) that the influence of temp steadies off at temps. $> 420^\circ\text{C}$. This is explained by the thermal cracking and the consequent formation of coke deposits. Fig. (8) is a plot of the Arrhenious equation. The method of least squares was used to calculate the coefficients:

$$\text{Ln } k = -10603.61 \frac{1}{T} + 21.67$$

$$E = 21.07 \text{ Kcal/mole}$$

This value corresponds well with that reported by Le Page (78). Fig. (7) illustrates the influence of pressure and it agrees with results obtained by Le Page (78) on other heavy distillates. The results on the influence of space velocity are shown in Fig. (5). The shape of the curves indicates that the reaction is of the second-order type. It is generally agreed that the kinetic order for hydrodesulfurisation of an oil containing a variety of sulfur compounds is second order. Thus at fixed hydrogen pressure the results showed a straight line logarithmic plot for sulfur removal against residence time. Equally at fixed flow rate H_2 pressure plotted against $\log(1/(1-x))$ gave approximately a straight line. The method of least squares was used to calculate the values of the velocity constants at different temperatures.

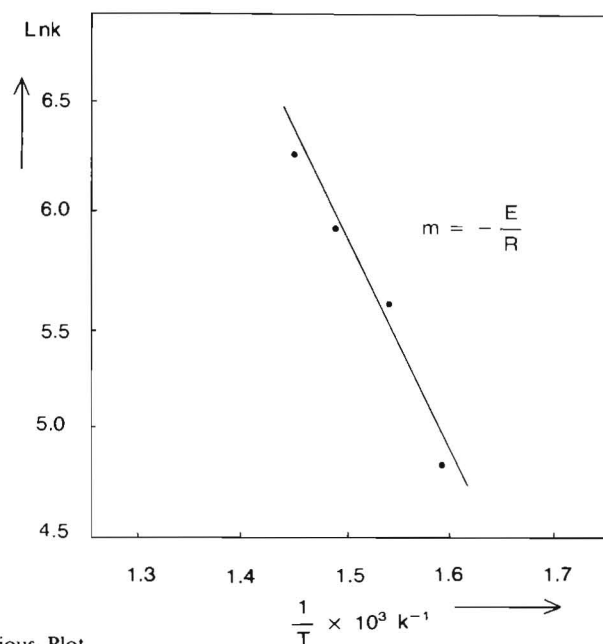


Fig. 8. Arrhenious Plot

5. Conclusions

The influence of the main operating variables such as temperature, space velocity and the pressure were investigated. Those were found to correspond well with industrial practice. The kinetics of the reaction was found to be of the second order type. More work should be carried out to investigate the effect of other variables such as the ratio H_2/HC , and the catalyst activity. Work will be carried out to investigate the more difficult problem of hydrodesulfurization of Syrian fuel oil which contains 5% sulfur using the same catalyst.

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إزاحة الكبريت بالهدرجة لزيت الغاز السوري فوق وسيط من أكاسيد الكوبالت مولبيدنوم

سعد الدين خرفان

قسم الهندسة الكيميائية - كلية الهندسة الكيميائية والبترولية - حمص - ص.ب: ١١٦٩ - سورية

إن إزاحة الكبريت من زيت الغاز عملية مهمة في صناعة التكرير السورية. ويستخدم هذا المركب في سورية على نطاق واسع في النقل وفي التدفئة في فصل الشتاء.

إن وجود نسبة مرتفعة من الكبريت في هذا المركب يؤدي إلى حدوث مشاكل تآكل وتلوث متعددة.

وتهدف هذه الدراسة إلى معرفة تأثير شروط التفاعل من حرارة وزمن بقاء وحفظ هيدروجين على كفاءة نزع الكبريت بالهدرجة من زيت الغاز فوق وسيط من الكوبالت - مولبيدنوم.

لقد تبين من الدراسة أن درجة الحرارة تزيد مردود العملية في المجال ٣٦٠ - ٤٢٠ م° ثم يتناقص التأثير بعد ذلك. كما وجد أن التفاعل من المرتبة الثانية وأن المردود يزداد بازدياد ضغط الهيدروجين حتى حدود معينة ثم يتضاءل التأثير بعد ذلك.

Costs of Electrical Interruptions in the Residential Area of Riyadh City

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ABSTRACT. Electrical service interruptions, caused by severe outages, and their impacts upon the residential consumers' sector in the city of Riyadh have been investigated. This study has been conducted through questionnaires distributed among selected residential consumers and their responses and opinions have been carefully analyzed. It has been found that this sector, which constitutes about 70% of the Saudi Consolidated Electric Company (SCECO) energy consumption, will suffer tangible and intangible losses should an outage occur in specific periods and last for a long time. Comparison with results of other studies is presented.

Electric service interruptions occur when system capacity, due to severe outages, is insufficient to meet the system load levels. During these periods of inadequacy, outage costs will be borne by the utility, its consumers and, perhaps, by society. The utility outage costs include loss of revenue, loss of future sales and increased maintenance and repair expenditure. These costs usually form only a small part of the total outage costs. The greater part is that borne by the consumers. The outage costs depend on many factors and situations, some of which are discussed in the following paragraphs.

The problem of estimating outage costs is affected by the perceived cost of an electric outage and the point in time when a consumer would like to buy electric energy but is unable to do so. Since there are different classes of consumers, each will tolerate loss of service differently. A residential consumer may suffer a great deal of hardship if an outage occurs during a hot summer day but it may be of little inconvenience to a commercial user which is forced to close until power is restored. Also an outage may cause a great loss to an industrial user if it occurs during the time of the production process. Therefore, consumers do not perceive service interruption to the same degree of hardship.

The outage costs to a particular consumer depend also on the alternatives available to that individual at the time of service interruption. If the outages are

not expected, the consumer may have very limited alternatives and may incur a great loss. On the other hand, if an adequate warning is given, the losses may be mitigated. Also, as an outage continues or spreads to a larger subset of society, the society cost will tend to increase and will include such indirect cost as effects of inconvenience, loss of products, food spoilage, health hazards, etc.

The major aspect of outage costs estimation is to assess the worth of power system reliability in order to compare it with the cost of power system reinforcement to establish the appropriate system reliability level. In this regard, it is important to realize that, while the evaluation of power system reliability has become a well established practice over the last decade, the assessment of the worth of reliability or conversely the estimation of costs of losses which result from system unreliability is still an immature technique. The major reason for this is that quantification of interruption costs is an intricate and often a subjective task.

A review of the literature reveals that the majority of approaches used to assess reliability worth are based on determination of the impacts of interruptions, *i.e.*, the cost of unreliability (Shipley *et al.* 1972, Telson 1975, Sullivan 1978, Mayers 1978, Manusinghe 1980, Bental *et al.* 1982, Sanghvi 1982, Wacker *et al.* 1983, Allan *et al.* 1986, Anderson *et al.* 1986, Juseret 1987, Billinton *et al.* 1987, Shaalan 1988). These approaches, however, are not strictly comparable, the major reason being that the scenarios and modeling techniques are not identical.

Methodology

The unmatched electric demand growth in the Kingdom of Saudi Arabia and the subsequent increase in system size, complexity and cost due to consolidations, reinforcements and interconnections have compelled the system to be more reliable (*i.e.* with the least outage occurrences).

The objective of this work is to explore the impact of outages upon the residential sector in the city of Riyadh. Riyadh is the capital of Saudi Arabia and the largest city within the SCECO'S service area. The methodology is thoroughly described and documented in (Shaalan and Albahrani 1988). This methodology represents a customer survey which is considered to yield relatively definite results and can estimate the real impact of energy shortages upon the various types of consumers, *e.g.* residential, commercial, industrial, etc. The survey is based on the type of dwelling, quality of service offered, history of service outages, degree of hardship and discomfort as a result of interruptions, the customer willingness-to-pay to avert an outage(s), impact of service interruptions at critical periods such as summer time and the holy month of Ramadan where the annual peak demand usually occurs.

Results and Discussions

The data used in this study is based on 354 responses from a residential survey resulting from 730 questionnaires (Shaalan and Albahrani 1988). The survey involved selected samples of residential consumers in Riyadh city. The respondents were asked to provide information concerning their monthly energy consumption and payment bill. This enables the cost estimation and other results to be related and analyzed for their relationship with household activities and type of dwellings. The breakdown of respondents by dwelling type and their average monthly energy consumption and electric payments are shown in Table 1.

Table 1. Respondents proportions, consumptions and payments by dwelling type

Dwelling type	% of respondents	Av. consump. (kWh/mo.)	Av. bill (SR/mo.)
Villa	67	4500	485
Duplex	12	2720	190
Apartment	21	2143	150

Opinions Regarding Electric Service and System Outages

In response to the attitudinal questions, there was an unanimity among the respondents that the rate of interruptions during the last two years was very low and the system offers a good and reliable service. A significant number of respondents reported no serious problems or monetary losses as a result of power failures.

Variation of Undesirability with Outages

To explore the extent of respondents' discomfort and anxiety during power interruptions, they have been asked to give, based on a scale varying from 0 (no undesirable effect) to 5 (extremely undesirable) their level of undesirability of not being able to use major electrical devices such as kitchen appliances, washing machines, entertainment equipment, airconditions, lighting, etc. Their varying responses are depicted in Figure 1. It is noticed from the figure that the most critical devices that the residential consumers will not be able to use should an outage occurs are mainly the airconditioners followed by lighting then kitchen facilities and washing machines. Entertainment came last on their preferences and usage priorities.

Variation of Undesirability with Frequency and Duration of Outage Occurrences

The survey suggests some hypothetical scenarios of power outages in summer time for 4 hours between 12 noon and 6 pm. These outages may occur once per

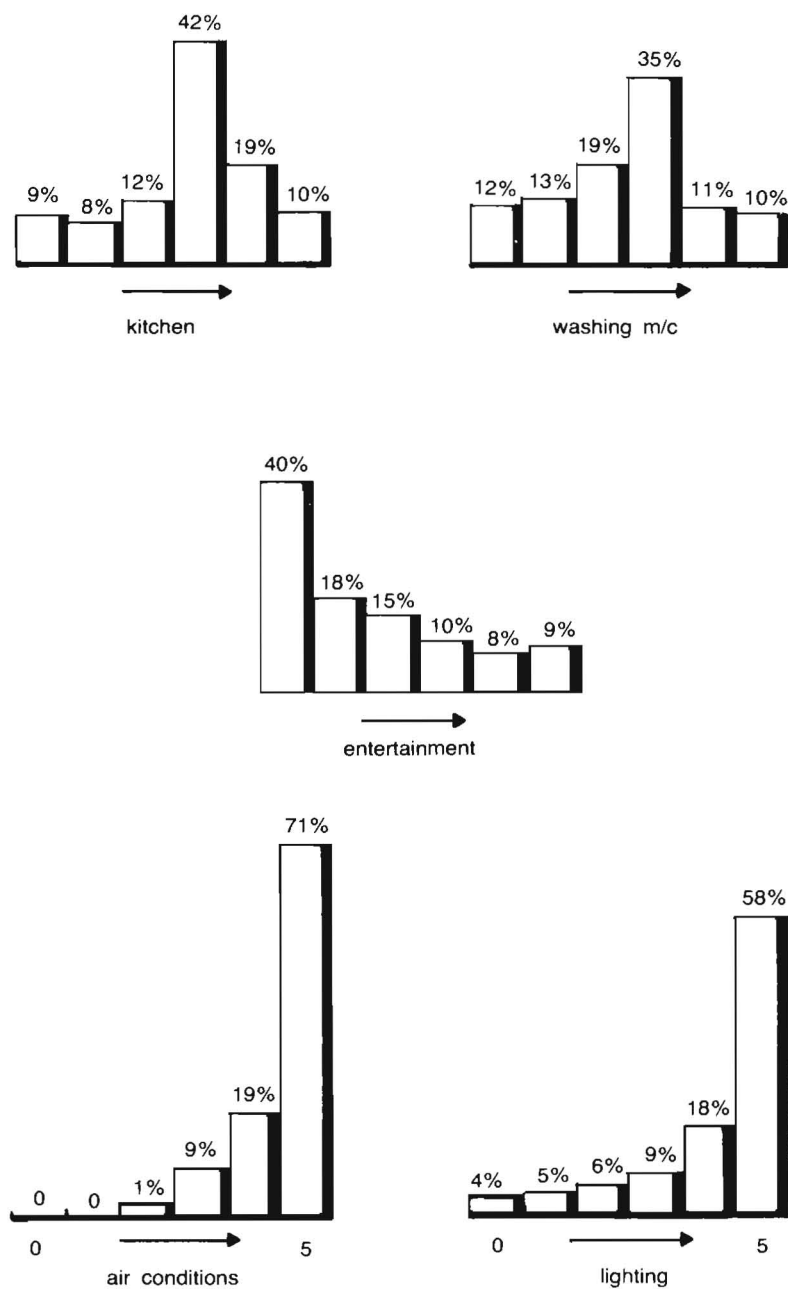


Fig. 1. Variation of undesirability with inability of using major electrical devices during electric outages.

year, month or day. Their opinions are shown in Fig. 2. From the figure, it is shown that the inconvenience and anxiety will directly increase with the frequency of the outages. The respondents' reactions towards duration and occurrence time of interruptions were sought. These occurrences were suggested to be in the summer season and after midday where the usage of air conditioning is mostly needed. The duration of these interruptions are suggested to be 20 minutes, 1 hour, and 4 hours. The results are shown in Fig. 3 which indicates that the respondents irritation rapidly increases with the length of interruption.

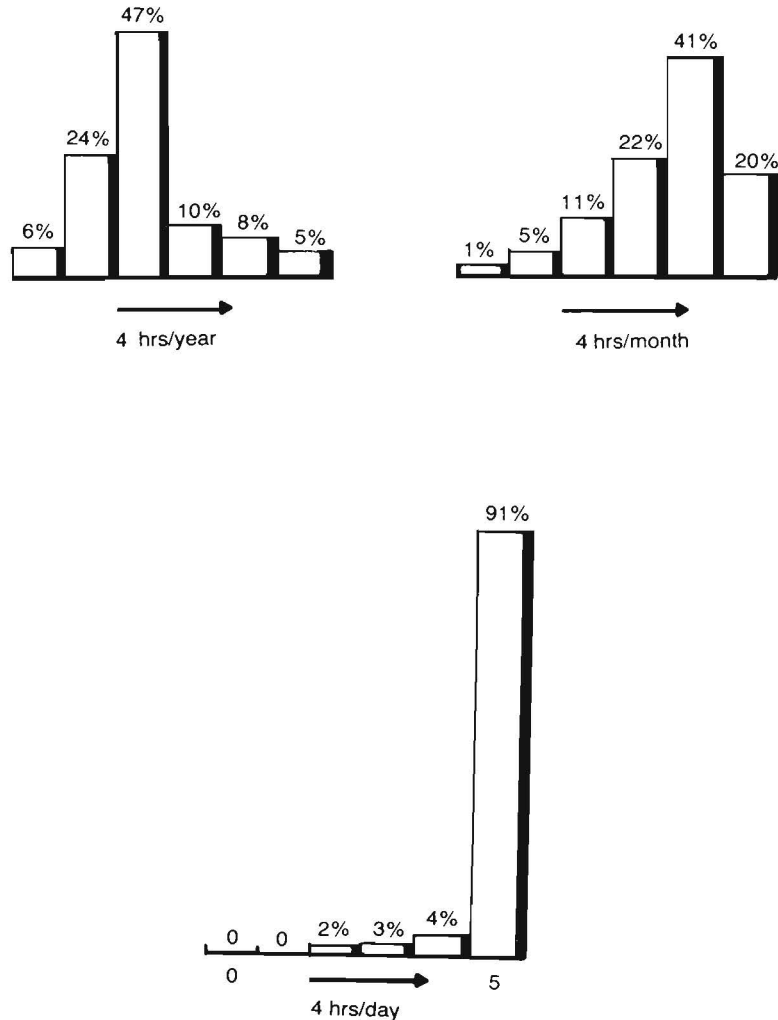


Fig. 2. Variation of undesirability with frequent outages occurrences.

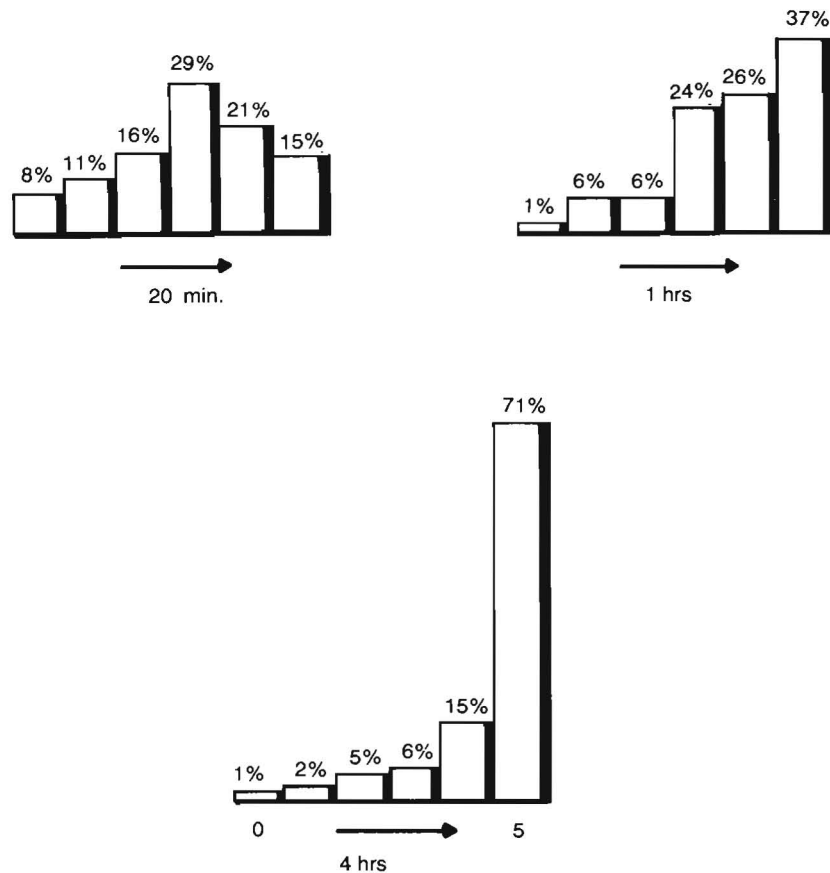


Fig. 3. Variation of undesirability with duration of outages.

Interruptions During Critical Periods

Ramadan is a holy and a spiritual month in the arabic calendar where Muslems observe fasting from dawn to sunset. The holy month of Ramadan is marked by higher energy consumption. This consumption is more pronounced when Ramadan concurs with summer time. This concurrence has been taking place for almost ten years, so the system annual peak load usually occurs in Ramadan. To measure the impact severity of interruptions during Ramadan and to compare it to other cases, the previous scenario has been considered. Fig. 4 portrays the extent of severity and hardship of interruptions occurring at midday of Ramadan. To compare the cases illustrated by Figs. 4 and 3, it is quite obvious that the interruptions are more immense and severe during the midday of Ramadan because of the high temperature in summer and the extreme usage of air-conditioners.

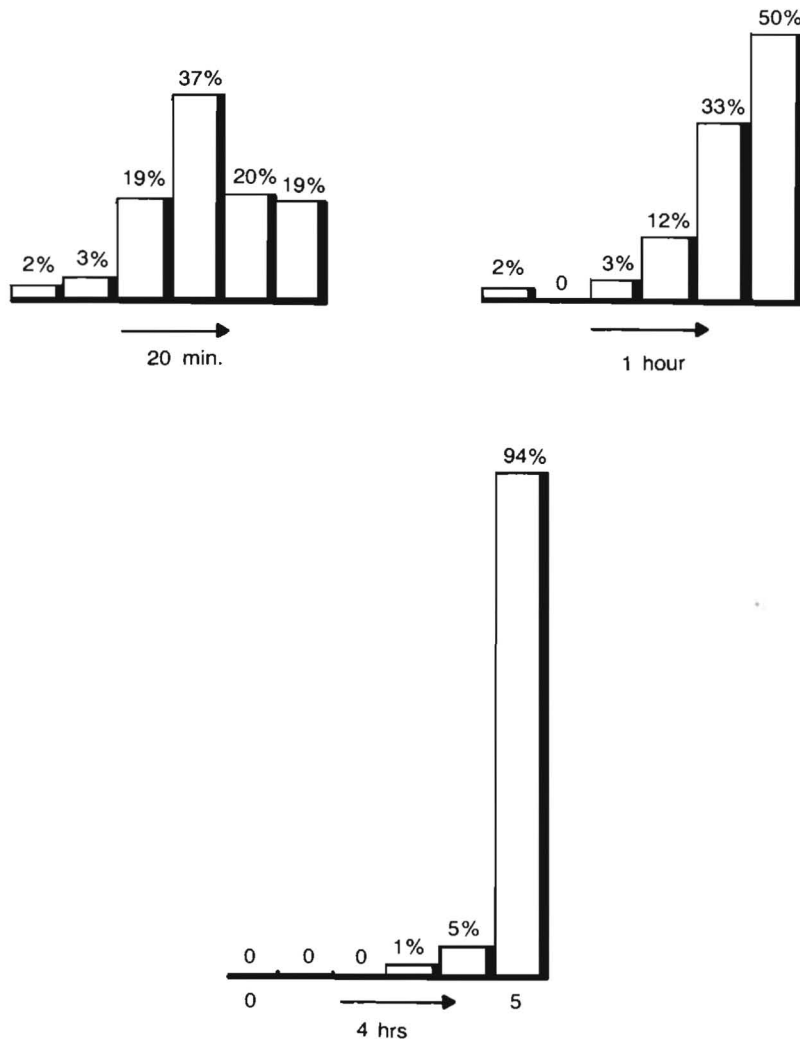


Fig. 4. Variation of undesirability with duration of outages in Ramadan

Costs Estimation Based on Willingness-to-pay Questions

As has been noticed so far, most of the outage effects are intangible and cannot be measured in terms of monetary values. Therefore, a single complete measure of the worth of reliability of supply to residential users is difficult if not impossible to obtain. The question that is appropriate to ask is: "Which set of estimations should an analyst use as a criterion of reliability worth?" The answer depends on the specific purpose and theoretical structure of the analysis. In general, it is the author's opinion that the most suitable estimate of reliability

worth is the willingness-to-pay. This approach is theoretically sound and more pertinent to the perception of the residential customer and to his needs.

The survey aims to measure the tendency among the respondents towards tariff increases and how much they are willing to pay to avoid interruptions. It is suggested that the power system has become subject to more frequent power outages. To increase system reliability, the company may add new generating units and/or reinforce its networks which may result in tariff increase. Hence, the question hypothesizes daily power interruptions in the summer period for durations of 20 minutes, 1 hour and 4 hours. The question then suggested a range of possible tariff rate increases and asked the respondents to perceive the interruption impacts and consequently to discern the fair and appropriate rate increases on top of the present tariff structure. The information reported by the respondents is displayed by Figure 5 which shows that a significant majority are willing to pay up to 20% of the present tariff to avoid the 4 hours per day interruptions. The willingness-to-pay (rate increase) becomes less when more rate increase is suggested or less frequent failures are postulated. The average value of the maximum amount per month that the respondents are willing to pay for a more reliable system is based on their average energy consumptions (kWh/mo.) and payments (SR/mo.) in summer time. The cost per interruption estimate for the residential sector as SR/kWh and SR/kW (kW is consumer's peak demand) are evaluated for comparison with other studies and for planning purposes. These are presented in Table 2. The SR/kWh estimates were weighted by the respondent monthly consumption and payment and converted to a per interruption basis to make the estimate consistent. The SR/kW was obtained by assuming a prevailing load factor of 21%. (SR/kW was converted to US\$/kW for comparison with other estimates).

Table 2. Residential outage costs estimation based on a daily interruption in summer time

Duration	SR/kWh	SR/kW	US\$/kW
20 minutes	0.2146	0.4507	0.12
1 hour	0.8048	1.6902	0.45
4 hours	4.3820	9.2022	2.45

(1 US\$ = 3.756 Saudi Riyal)

Limitations of the Results

The interruption costs estimations seen in Table 2 were analyzed (SAS 1982) for variation of the mean with the respondents' answers to the willingness-to-pay question, attitudinal, frequency and duration of interruptions, and consumption and payment variables. However, there are some potential limitations for the survey results, and these can be summarized as follows:

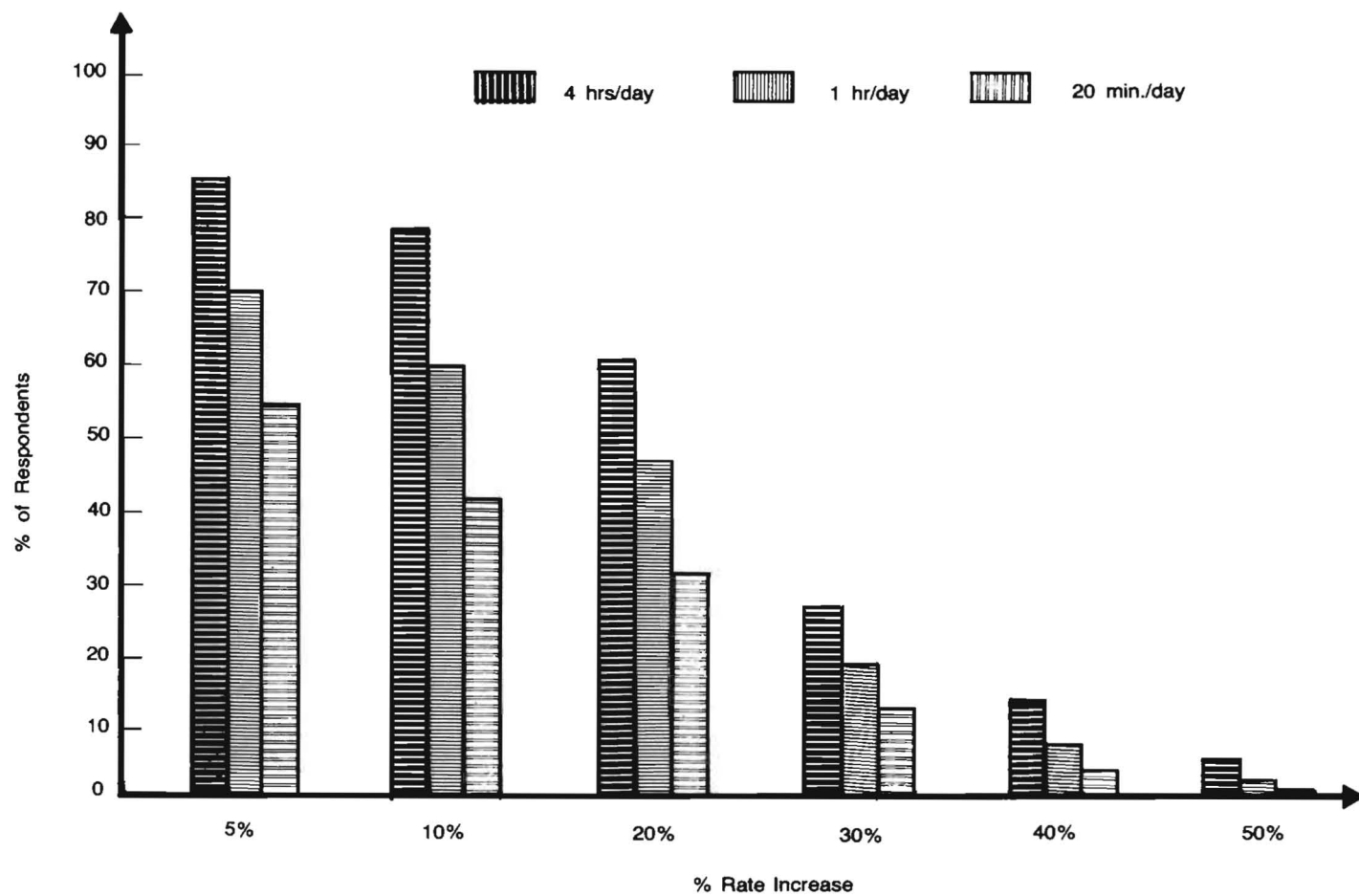


Fig. 5. Rate increase as a function of outages frequency and duration.

- 1) The reliability level for the SCECO'S system is very high and the respondents have probably not experienced serious power interruptions for the last two or more years. Therefore, their predictions of the actual damage that an outage will cause may differ.
- 2) Only limited scenarios have been proposed, *i.e.*, more interruptions and longer durations could be anticipated.
- 3) There is a possibility that those who did not respond to the survey hold different opinions.
- 4) A number of responses were rejected due to lack of usable information.

Comparison of Results with Previous Studies

Figure 6 displays the outage frequency and duration cost estimations obtained by this study (Riyadh), Koval *et al.* 1979, Sweden 1981, Wacker *et al.* 1983, Billinton *et al.* 1987. Wacker *et al.* and Koval *et al.* used indirect worth evaluation based on the preparatory actions the consumer may take during interruptions. Billinton *et al.* relate the costs to the expected energy not served by using a frequency and duration approach and Monte Carlo simulation. The Swedish study determined the residential losses on the basis of household activities and leisure time. The comparison indicates that Riyadh study has yielded estimates rather below those of the other studies. This can be postulated as the methodology was in essence based on the actual payable tariff. The government heavily subsidises the private electric industry (the SCECOs) and the consumer pays only a reasonable part of the cost. In this respect, it is believed that the tariff in Saudi Arabia is much lower than those of other countries. The differences in estimations, seen in Figure 6, are attributed to variations in system characteristics, the non-linear nature of the outage costs and the different techniques employed.

Conclusions

This paper presents a summary of research conducted to evaluate the perceived costs incurred by the residential consumers in the city of Riyadh due to power service interruptions. The analysis reveals that the interruptions result partly in consumer's discomfort and inconvenience which are difficult to quantify in monetary values. Using a willingness-to-pay approach, cost estimations of SR 0.4507, SR 1.6902 and SR 9.2022 per kW for 20 min, 1 hour, and 4 hour daily interruptions, respectively, have been determined. These figures imply the non-linearity of outage costs. The major contribution of this work is the improvement of the outage costing methodology. Another significant contribution is the compilation of residential cost of outages information which is a key input to reliability-based power system planning and comparison with results of other researchers.

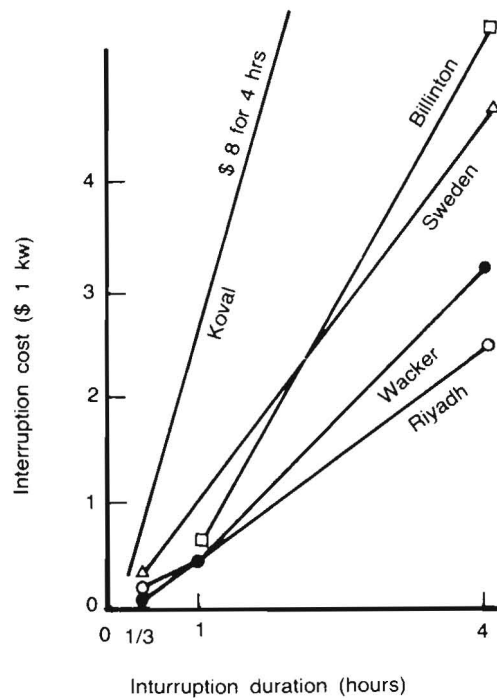


Fig. 6. Comparison of residential outage cost of Riyadh with other studies

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تقدير تكاليف الانقطاعات الكهربائية عن قطاع المستهلك السكني بمدينة الرياض

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قسم الهندسة الكهربائية - كلية الهندسة - جامعة الملك سعود - ص.ب ٨٠٠ الرياض ١١٤٢١
المملكة العربية السعودية

تم في هذا البحث دراسة الآثار المترتبة عن إنقطاعات الخدمة الكهربائية عن المستهلك السكني بمدينة الرياض. ولقد أجريت هذه الدراسة بواسطة استبيانات وزعت على عينات منتخبة من المستهلكين السكنيين حيث تم تحليل ودراسة استجاباتهم وآرائهم بكل عناية. ولقد ظهر من الدراسة أن هذه الفئة من المستهلكين - والتي تشكل حوالي ٧٠٪ من مجمل استهلاك الطاقة بمنطقة الشركة السعودية الموحدة للكهرباء (سكيكو) - ستمنى بخسائر مادية ومعنوية إذا حدث انقطاع في فترات معينة واستمر وقتاً أطول. وحيث أن المعاناة المعنوية من الصعب تفسيرها على شكل قيم مالية، فقد ظهر من الدراسة أن الخسائر المادية قد تصل إلى أربعة ريالات لكل كيلوات ساعة وتسعة ريالات لكل كيلوات عند حدوث الإنقطاع في فصل الصيف. كما تمت مقارنة نتائج هذه الدراسة بنتائج دراسات أخرى.