

Sorption Enhanced Methanation: A Study on Reactor Configuration and Sorption Effects on the Sabatier Process

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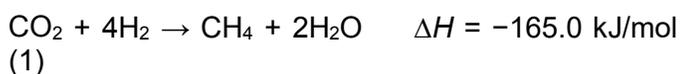
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Abstract: A sorption enhanced methanation process was investigated using a 40Ni/Al₂O₃ (γ) catalyst along with zeolite 4A and lanatanaBa sorbents. Effects of reaction conditions, reactor configuration and the effect of sorbent on the catalytic reaction were tested in a fully-automated lab scale pilot plant. Results were quantified in terms of CO₂ conversion and CH₄ yield. Mass balances were performed to observe the effects of regeneration and reuse of the sorbents. The sorption enhanced methanation process using zeolite 4A as the sorbent showed heightened selectivity towards the CH₄ product. Water-based mass balances on sorption-desorption cycles confirmed the viability of continuous regeneration and reuse of the catalytic bed and sorbent. Errors in calculated mass balances and conversions mainly result from propagation of inaccuracy in measurement of mass of water at the outlet of the reactor and the transient kinetics of the reaction upon introduction of reactants.

Introduction

Fossil fuels and natural gasses have limited quantities and their use contributes to the increase of greenhouse gasses in the atmosphere; therefore, processes that utilize renewable resources are of vital importance. Recently, renewable processes for the production of H₂, such as those that utilize renewable energy to perform electrolysis reactions, have shown promise. That said, the current gas grids in the United States and Europe are built to support natural gas. Through use of H₂ produced by renewable energy and CO₂, the Sabatier process can be used to generate renewable methane for use in the pre-existing natural gas grid. Utilization of renewably produced H₂ creates a closed carbon cycle, where the total accumulation of CO₂ in the atmosphere resulting from the combustion of methane is zero. The Sabatier reaction is given in Equation 1.



Although the catalyzed reaction can achieve high yields, the evolution of the toxic byproduct CO along with the need for high operating temperatures (300 – 400 °C) and pressures are still issues that need to be solved before the reaction is used industrially.^[1,2] By uptaking water produced by the reaction, the equilibrium is shifted towards the products, thus reducing the evolution of CO and enabling a lower-pressure process to achieve high yields. This process is commonly known as the sorption enhanced methanation process. Additionally, evolution of CO is minimized at lower operating pressures and temperatures. The sorption enhanced process is based off of Le Chatelier's principle and is known as sorption enhanced methanation. In this study, sorption enhanced methanation is investigated using a 40Ni/Al₂O₃ catalyst mixed into a bed of zeolite or lantanaBa absorbent. Zeolite has been chosen for use in this process due to its high sorption capacity and potential for use as a catalyst support.^[3,4] Despite research based on a wide range of active metals, Ni based materials remain the highest-performing

catalysts when selectivity, efficiency and cost are considered.^[2] The combination of zeolite and Ni catalyst is a promising mixture for use in the sorption enhanced methanation process.

Literature Review

Although catalysis of the Sabatier process has been extensively studied, the evolution of a toxic CO byproduct remains an issue. Some studies have shown a methane selectivity of up to 99% with no sorbent when using Ni-Al alloys or Ni₁₆ as catalysts, yet in most cases the process only exhibits selectivity between 80 and 95 % at pressures below 20 bar.^[5] Likewise, recent research has shown promising results using commercial Ni catalysts coupled with zeolite based materials as sorbents. Borgschulte et al.^[6] studied the sorption enhanced methanation process using Ni particles dispersed on a zeolite 5A matrix at different Ni loadings in a tubular flow reactor. A peak Ni loading of 2.5 at% was observed and used in experiments. The zeolite sorbent was reported to completely eliminate the evolution of CO while simultaneously improving methane yield for limited time periods. At 170 °C and hydrogen flow rate of 50 ml min⁻¹ the reaction was found to have a 100 % selectivity toward methane before the saturation of the adsorbent. After the sorbent was saturated, CO was produced and CO₂ conversion decreased.^[6] The transient kinetics prove the sorption enhanced methanation concept and show the benefits of sorbent enhanced catalysis in the Sabatier process. The existence of a peak Ni loading in zeolite suggests that the dispersion of catalyst amongst adsorbent plays an important role in reaction kinetics. In a similar study by Walspurger et al.^[7], a conversion of close to 100 % was demonstrated at pressures as low as 10 bar and a temperature of 300 °C. The catalytic bed consisted of a 1:5 ratio of propriety Ni catalyst to Zeolite 4A.^[7] The sorbent showed the potential for a process yielding grid quality SNG at pressures as low as 10 bar as opposed to 60 bar, leading to compression energy savings of up to 40 percent. A study by Delemelle et al.^[8] also showed that the sorption enhanced methanation process can have CH₄ selectivity of up to 100 % using Ni catalysts supported on commercial zeolite sorbents LTA and LTX by wet impregnation. The effect of sorption on the process was not quantified against that of the catalyst alone. A support pore size of equal to or larger than 5A was found to enhance the selectivity

towards CH₄.^[8] It is clear that high selectivity towards methane can be achieved through sorption enhanced methanation, yet further studies are needed to quantify the effect of the sorbent on the reaction.

Methods

All materials used in the catalytic bed were first pressed to 10 tons then crushed with mortar and pestle and sieved to particle size between 42 and 50 microns. The catalyst used in the study was 40 weight percent Ni loaded on gamma alumina (40Ni/Al₂O₃ (γ)) and was prepared by wet impregnation. The two adsorbents tested were zeolite 4A (Molecular Sieves, 4A, Sigma-Aldrich) and a lanthanum-barium based sorbent, hereafter referred to as lanatanaBa, prepared by wet impregnation. The catalyst and adsorbents were calcined at 700 °C for 7 hours. Fine silicon carbide (Sigma-Aldrich CAS 409-21-2) was mixed into the catalytic bed in order to adjust bed length and prevent hot spots. All experiments were performed in a stainless-steel tubular flow reactor of diameter 13 mm. The mass of catalyst used in each experiment was 0.35 g. The reactor was configured with two thermocouples: one before the catalytic bed and one inside of the catalytic bed. The temperature of the first thermocouple was used to control the temperature of the reactor. Figure 1 gives a schematic representation of the reactor configuration.

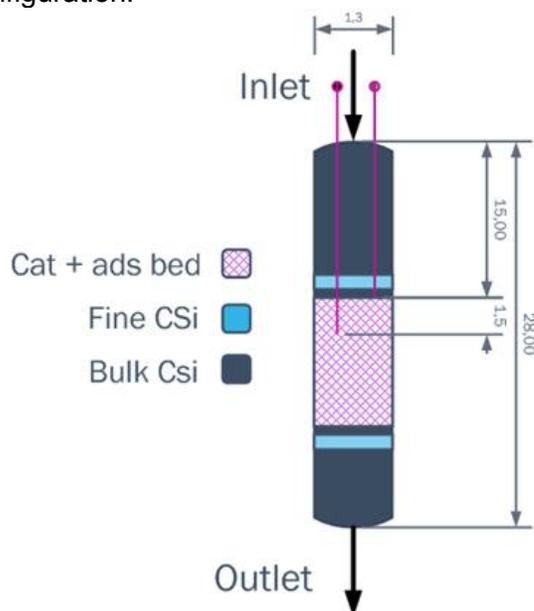


Figure 1: Dimensions and configuration of the reactor used in experiments.

The typical mass of adsorbent used was 2.1 g with the exception of one experiment in which 7.2 g was used. The gas flow, temperature, and pressure were controlled by a fully-automated lab-scale pilot plant. Temperature, pressure, bed length and weight hourly space velocity (WHSV) were varied in order to find optimal conditions for experiments. Sorption experiments were performed at temperatures of 300 and 325 °C and pressures of 10 and 15 bar. WHSV was varied between 26 and 80 (g gas g catalyst⁻¹ h⁻¹). In each experiment, the ratio of volumetric flow of CO₂ to H₂ at the inlet of the reactor was 1:4.

The product stream of gases was analyzed by an in-line GC-TCD using N₂ as an internal standard. The concentrations of H₂, CH₄, N₂, and CO₂ were measured using the in-line GC-TCD at the reactor outlet. N₂ flow was measured manually before and after each experiment. The composition of the inlet stream was measured directly following each experiment by bypassing the reactor. In each experiment, the reactor was allowed to reach reaction conditions under a flow of only the N₂ internal standard, then the reactant gases were introduced one-by-one roughly one minute before

the first GC measurement was recorded. The gaseous water produced by the reaction was removed from the product stream using a Peltier condenser before the gases were analyzed. The production of water was monitored by measurement of the mass of water condensed by the condenser.

All desorption cycles were carried out by heating the reactor to 450 °C at atmospheric pressure under a constant stream of N₂ at 100 Nml min⁻¹. The reactor was allowed to return to reaction conditions under a flow of 42 Nml min⁻¹ of nitrogen before reactants were introduced for the following absorption cycle.

Results

Reactor temperature, inlet flow rate, and bed length were all varied in order to determine optimal reactor configuration and reaction conditions. Table 1 shows a summary results from each experiment performed, where yield of CH₄ is defined as the fraction of CO₂ fed to the reactor that produced CH₄. Results shown in Table 1 are representative of steady state conditions, where the adsorbent is considered saturated.

Table 1: Summary of each experiment performed showing reaction conditions, bed length, and steady state conversion results.

Reactor Temperature (°C)	Absorbent	Total Inlet Flow (Nml/min)	Pressure (bar)	Bed length (cm)	Bed Temperature (°C)	Conversion CO ₂ (%)	Yield CH ₄ (%)
275	None	800	10	1	299	4	--
	LantanaBa	800	10	3	290	4	4
	None	800	3	--	290	15	2
	None	895	10	5	288	6	4
300.00	LantanaBa	800	10	3	318	10	11
	lantanaBa	272	15	3.3	308	33	29
	Zeolite 4A	265	15	4	306	33	37
	None	265	15	4.9	303	0.88	3.03
	None	895	10	5	306	5	0.85
	None	895	10	5	323	13	13
	Zeolite 4A	867	15	5	305	33	35
	Zeolite 4A	263	15	10.1	305	2	1
	None	895	10	11.2	306	5	0
	None	895	15	11.2	306	7	0
325.00	None	800	2	--	432	74	63
	Zeolite 4A	496	10	3.8	350	85	86
	None	265	15	4.9	327	5.58	6.51
	Zeolite 4A	867	10	5	361	77	81
350.00	None	800	3	--	461	76	64
	None	265	15	4.9	352	16	14
	None	895	10	5	444	76	82

As seen in Table 1, the reaction conditions and bed length have a substantial influence on conversion of CO₂ and yield of CH₄. A catalytic bed with shorter length was observed to have a higher temperature. Physically, we believe this to be a product of the heat of reaction. When the catalyzed reaction takes place in a more concentrated space, the heat produced is concentrated into a smaller area, thus elevating the temperature of the bed above that of the set point. When the catalyst is dispersed throughout a longer bed, the bed temperature is observed to be lower and more controlled. Since the reaction kinetics are highly dependent on temperature, the difference in bed temperature has a large influence on conversion and yield. In experiments with bed length lower than 3 cm, the heat of reaction became so great at temperatures over 300 °C that the temperature of reaction could not be controlled. In future absorption experiments, bed length, pressure, and temperature will be held constant.

In adsorption experiments, water breakthrough time using 2.1 g of sorbent is observed within the first 6 to 12 minutes of the experiment. The water breakthrough time indicates saturation of the sorbent and thus marks the end of the sorption enhanced process. After water breakthrough, the reaction is no longer affected by the sorbent, at which point a decrease in the yield of CH₄ should be observed as the shift in equilibrium is reversed. The minimum sampling time of the GC is 4 minutes. Upon introduction of reactants, the reactor experiences a transient period of 10 - 20 minutes. Therefore, the effect of adsorbent could not be quantified from experiments that used 2.1 g of sorbent. Figure 2 shows the transient behavior of the reactor along with conversion of CO₂ and yield of CH₄ as a function of time.

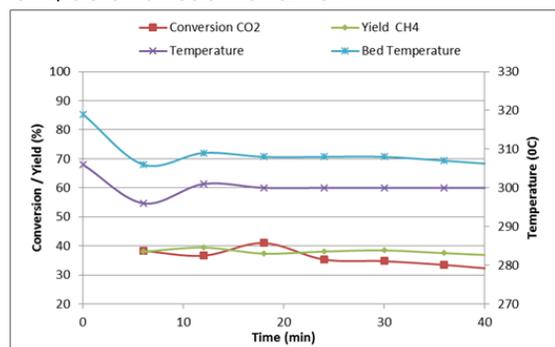


Figure 2: Reactor temperature, CO₂ conversion, and CH₄ yield as a function of time showing the transient behavior of the reactor upon introduction of gasses.

One final experiment was completed using 7.2 g of zeolite 4A with the same amount of catalyst as the other experiments in order to observe the effect of zeolite 4A on the reaction. The total flow of gasses at the inlet of the reactor was 263.5 Nml min⁻¹ at a temperature of 300 °C and pressure of 15 bar. The conversion of CO₂ during the experiment shows a decreasing trend with time as the zeolite becomes saturated. During the sorption enhanced methanation cycles, no CO byproduct was detected by the GC. Under the same reactor configuration and conditions without absorbent the CO byproduct is present. Figure 3 shows the conversion, and reactor temperature during the first absorption cycle along with the status of the sorbent. The conversion is slightly higher before breakthrough of water is observed. At a stable reactor temperature and pressure, the conversion of CO₂ before breakthrough is 25.55±0.75 %. After breakthrough, the conversion decreased to 22.15±0.54 %.

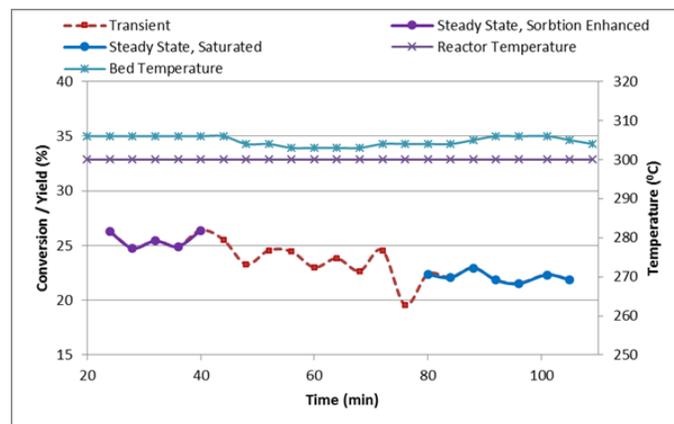


Figure 3: CO₂ conversion and reactor temperature during the first absorption cycle showing the regions of steady state conversion during sorption and saturation.

Mass balances on water were carried out for each experiment that used absorbent. The breakthrough time was defined as the time period in which the level of the condenser remained constant. From the mass balances it can be confirmed that the sorbent is absorbing the water byproduct before saturation. An example mass balance is given in Table 2, where theoretical water produced is calculated by averaging the CH₄ outflow measured by the GC during the experiment and multiplying it by the total time that the reaction took place. The water desorbed was measured with a scale and is taken as the difference in water measured before

Table 2: Water mass balance for two cycles of absorption and desorption using lantanaBa.

Overall mass balance (water)	Theoretical Produced (g)	Measured Water (g)	Water in vapor (g)	Balance (g)	Water desorbed (g)	Remainder (g)	Desorbition %
Cycle 1	1.46	1.09	0.00	0.37	0.36	0.01	96.39
Cycle 2	1.95	0.91	0.00	1.04	0.84	0.20	80.92
Total	3.41	2.00	0.01	1.41	1.20	0.21	84.97

and after desorption. In a time period of 1 hour, 80 to 100 % of water absorbed by the zeolite is desorbed. Due to large errors in measurement of water by the scale and the approximation of water produced, large errors may contribute to inconsistencies in the mass balance. Conversion and selectivity during the first and second absorption cycles remained constant, confirming the viability of continuous regeneration and reuse of the catalytic bed during sorption enhanced methanation.

Discussion

Due to the long transient period of the reactor upon introduction of reactants, future experiments should be carried out with larger concentrations of sorbent in the bed in order to more clearly quantify the effect of the sorbent. With more sorbent, the catalytic bed can have more length and the reaction temperature can be better controlled. Furthermore, the results suggest that a total inlet flow of gasses should exceed 450 Nml min^{-1} . In experiments at $325 \text{ }^\circ\text{C}$ with total inlet flow above 450 Nml min^{-1} , conversion of CO_2 is consistently above 70 % regardless of pressure. Conversely, with a total inlet flow of 265 Nml min^{-1} and pressure of 15 bar the conversion is less than 6 %. This dramatic difference in conversion may be due to the turbulence of the flow. In laminar flow regimes, the rate of reaction may be limited by mass transfer. That said, more research is needed to prove this theory, as a longer retention time would favor reaction kinetics.

Qualitatively, the results show proof of concept for the sorption enhanced process. In all trials using catalyst with no sorbent CO is evolved. The evolution of CO remains prevalent even at high conversions of CO_2 . During the sorption enhanced process using 7.2 g of sorbent, CO was measured, but was not detected by the GC indicating that selectivity towards CH_4 was close to 100%. This result was observed in both the first active period of absorption and the second absorption cycle after regeneration of the sorbent. Further experiments are needed to quantify to the full extent the differences

in yield and selectivity of the sorption enhanced process to those of the catalytic process alone.

The distribution of the catalyst among the zeolite absorbent may also have dramatic effect on the sorption enhanced reaction. In this study, the catalyst and sorbent existed as separate particles of diameter 42 - 50 microns. In this configuration the sorbent acts on the reaction system as a whole. If the zeolite and catalyst were pelletized and sieved as a mixture, the heightened catalyst surface area and the close proximity of catalyst to zeolite may have a tangible effect on reaction kinetics. Under this configuration, the sorption would happen locally at the reaction centers, instead of altering the overall environment of the reactor.

Inconsistencies in the mass balances can be traced back to errors in the measurement of water coming out of the reactor. Although the scale used is accurate to $\pm 0.0001 \text{ g}$, the scales accuracy is lessened by the experimental setup. The outlet for water was inserted into a collection bottle through a parafilm covering and the bottle was placed on the scale. During experiments, the mass of the scale while no water was exiting the reactor could be seen varying in measurement up to $\pm 0.2 \text{ g}$. In any given experiment, the amount of water produced ranged between 0.5 and 1.5 g, introducing errors of up to 40 % in the mass balance of water. Errors in conversion are also large upon introduction of reactants due to the transient temperature and kinetics of the reaction during the first 10 to 20 minutes.

Conclusion

Reactor configuration, reaction conditions, and the effect of sorbents on the Sabatier process has been investigated. Optimal reactor configuration and reaction conditions for future sorption-based experiments have been identified. The sorption enhanced process has been found to mitigate the evolution of CO when compared to the catalytic process alone, and the sorbent has been proven effective during multiple sorption and desorption cycles. Further research is needed in the field of

sorption enhanced methanation to quantify the effects of catalyst dispersion, sorption effects and reaction conditions. That said, the sorption enhanced methanation process has high potential for use in storage of excess energy in the form of methane and creating a carbon neutral energy production and consumption cycle.

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We would like to thank our referees for their dedication to the integrity of the journal. Referees ensure that the published research is of the highest caliber. The journal's rigorous peer-review process is dependent on the referees' expertise. We would like to thank the following 2018-2019 referees: Cordi Craig, Dr. Edward M. Schoolman, Dr. Katharine J. Schweitzer, Dr. Richard Plotkin and Dr. Charles Coronella.



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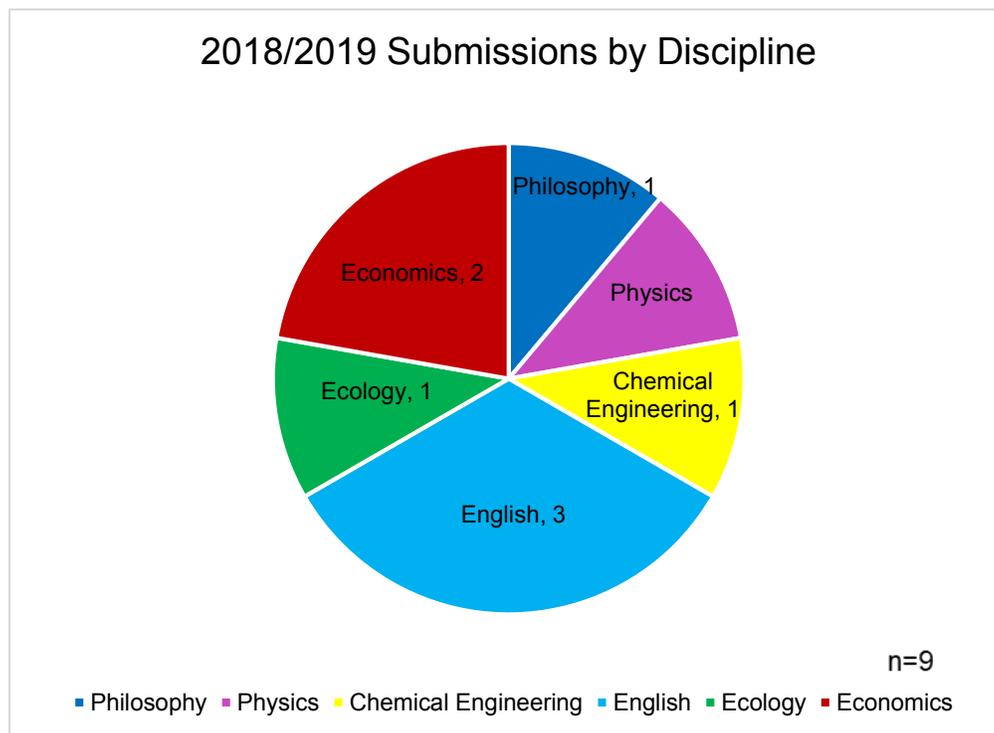
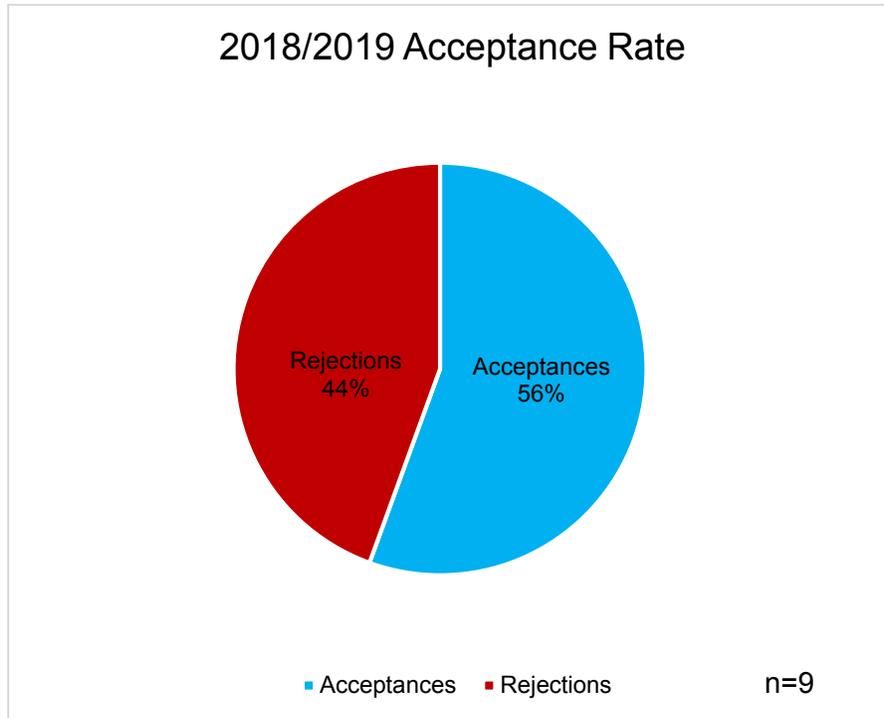
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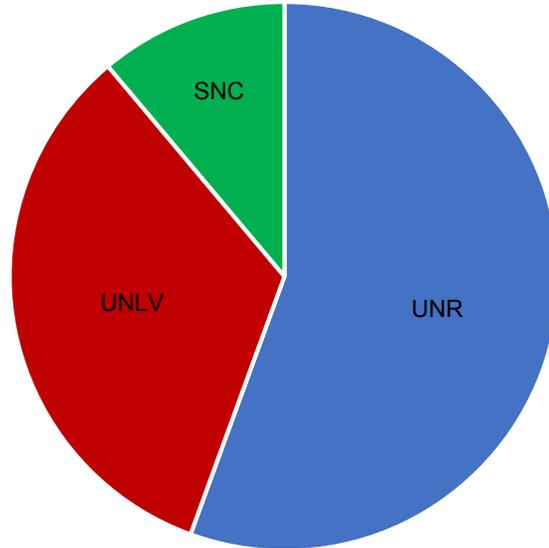


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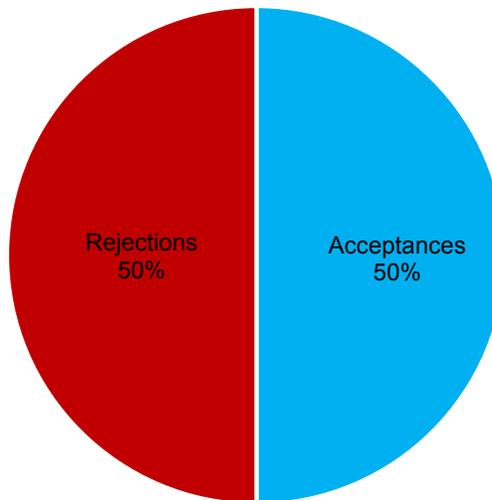
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